

SUPPORTING INFORMATION

Supporting Information

Optical Resolution of 1,16-Dihydroxytetraphenylene by Chiral Gold(III) Complexation and Its Applications as Chiral Ligands in Asymmetric Catalysis

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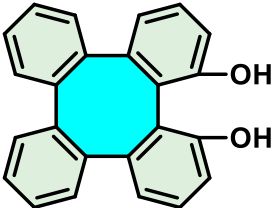
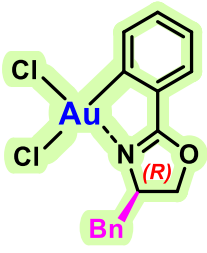
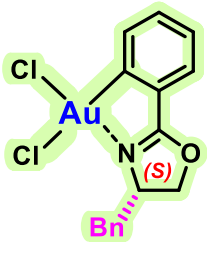
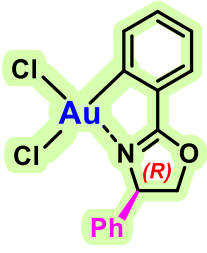
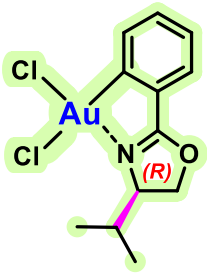
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General Methods

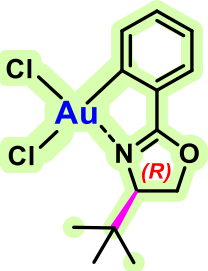
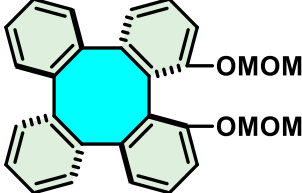
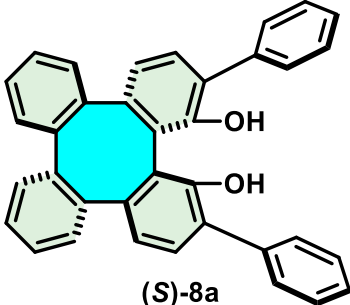
Unless otherwise noted, reagents and solvents were purchased from commercial sources and used without further purification. (±)-1,16-Dihydroxytetraphenylene (**DHTP**) were synthesized according to literature procedure (*Synthesis*, **2017**, *49*, 181-187). Enantiopure oxazoline-based cyclometalated gold(III) dichlorides were synthesized according to literatures (*Angew. Chem. Int. Ed.*, **2017**, *56*, 3074-3079; *Org. Lett.*, **2019**, *21*, 6289-6294). Potassium alkynyltrifluoroborates were prepared according to literatures (*Org. Lett.*, **2020**, *22*, 7427-7423; *Org. Lett.*, **2013**, *15*, 5052-5055). Allylic alcohol substrates were prepared according to literatures (*Angew. Chem. Int. Ed.*, **2012**, *51*, 3470-3473; *Synthesis* **2015**, *47*, 976-984; *Synthesis*, **2011**, 2600-2608). Thin layer chromatography was performed on precoated silica gel 60 F²⁵⁴ plates. Flash column chromatography was performed using silica gel (200-300 mesh). ¹H NMR and ¹³C NMR spectra were recorded on Bruker AscendTM 400 and AscendTM 600 spectrometers. Chemical shifts (ppm) were referenced to TMS and coupling constants are given in Hz. Data for ¹H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; brs, broad singlet; d, doublet; dd, double doublet; ddd, double-double doublet; t, triplet; td, triple doublet; tt, triple triplet; q, quartet; qd, quadruple doublet, m, multiplet), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). Data for ¹⁹F NMR and ³¹P NMR were reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained on Thermo Scientific Q Exactive, or Waters Xevo G2-XS QToF spectrometers. X-ray crystallographic data were recorded on Bruker D8 VENTURE. High pressure liquid chromatography (HPLC) analyses were performed on Agilent 1260 Infinity II equipped with chiral column from Daicel[®]. Circular dichroism (CD) spectra were measured on an Applied Photophysics Chirascan spectrometer. Melting points (mp) were determined on an SGW X-4A microscopic melting point apparatus. Optical rotations were recorded on a Rudolph Automatic Polarimeter. IR spectra were collected on Bruker VERTEX 70v and Bruker VERTEX 80v spectrometers. Known compounds were characterized by comparison of their ¹H, and ¹³C NMR spectra the previously reported data.

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Table S1 References of Key Known Compounds Used in this Article

Compounds	References
 <p>(±)-DHTP</p>	<p>a) J.-F. Wen, W. Hong, K. Yuan, T. C. W. Mak and H. N. C. Wong, <i>J. Org. Chem.</i>, 2003, 68, 8918-8931;</p> <p>b) J.-F. Cui, H. Huang and H. N. C. Wong, <i>Synlett</i>, 2011, 1018-1022;</p> <p>c) G.-L. Chai, J.-W. Han and H. N. C. Wong, <i>Synthesis</i>, 2017, 49, 181-187.</p>
 <p>(R)-3</p>	<p>J.-F. Cui, H.-M. Ko, K.-P. Shing, J.-R. Deng, N. C.-H. Lai and M.-K. Wong, <i>Angew. Chem. Int. Ed.</i>, 2017, 56, 3074-3079.</p>
 <p>(S)-3</p>	<p>J.-F. Cui, H.-M. Ko, K.-P. Shing, J.-R. Deng, N. C.-H. Lai and M.-K. Wong, <i>Angew. Chem. Int. Ed.</i>, 2017, 56, 3074-3079.</p>
 <p>(R)-3b</p>	<p>J.-F. Cui, H.-M. Ko, K.-P. Shing, J.-R. Deng, N. C.-H. Lai and M.-K. Wong, <i>Angew. Chem. Int. Ed.</i>, 2017, 56, 3074-3079.</p>
 <p>(R)-3c</p>	<p>J.-F. Cui, H.-M. Ko, K.-P. Shing, J.-R. Deng, N. C.-H. Lai and M.-K. Wong, <i>Angew. Chem. Int. Ed.</i>, 2017, 56, 3074-3079.</p>

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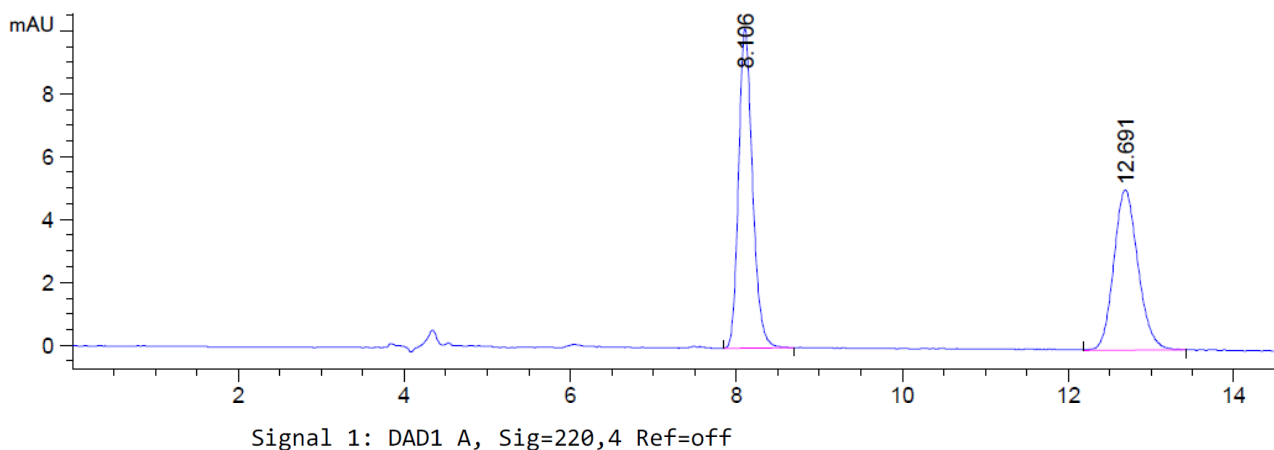
 <p>(R)-3d</p>	<p>J.-J. Jiang, J.-F. Cui, B. Yang, Y. Ning, N. C.-H. Lai and M.-K. Wong, <i>Org. Lett.</i>, 2019, <i>21</i>, 6289-6294.</p>
 <p>(S)-5</p>	<p>H. Huang, T. Stewart, M. Gutmann, T. Ohhara, N. Niimura, Y.-X. Li, J.-F. Wen, R. Bau and H. N. C. Wong, <i>J. Org. Chem.</i>, 2009, <i>74</i>, 359-369.</p>
 <p>(S)-8a</p>	<p>G.-L. Chai, B. Zhu and J. Chang, <i>J. Org. Chem.</i>, 2019, <i>84</i>, 120-127.</p>

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Experimental Procedures

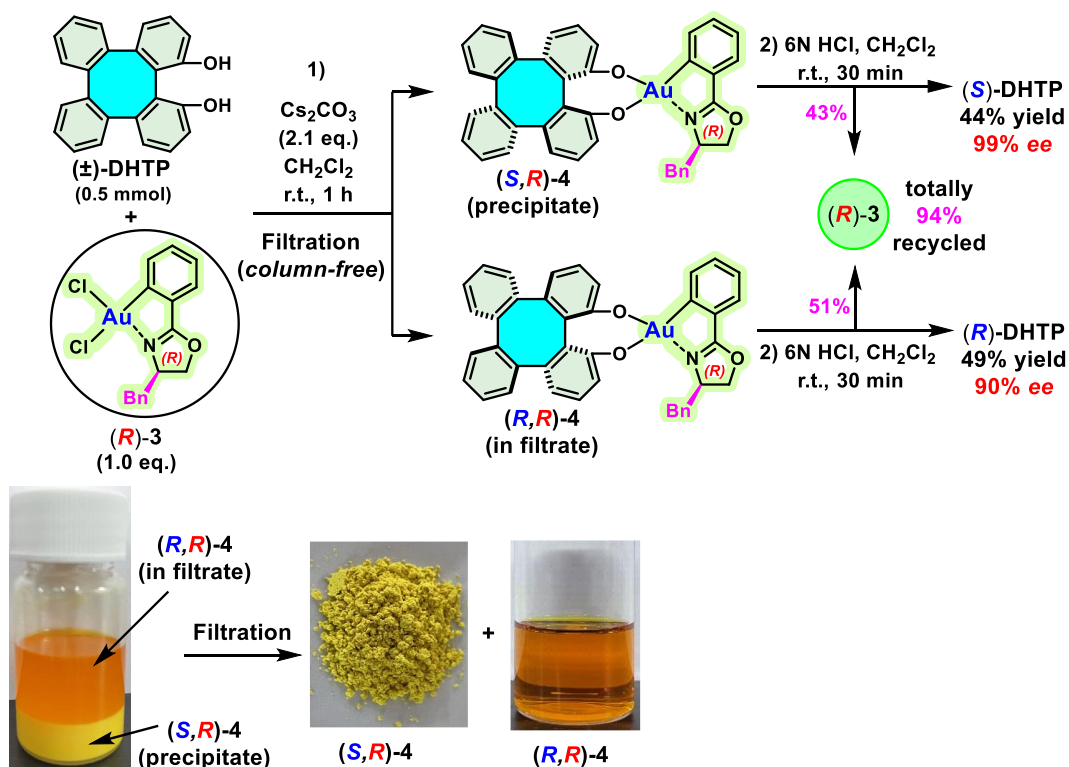
HPLC spectrum of (\pm)-DHTP:

Daicel Chiralpak[®] AD-H, 40% *i*PrOH, 60% hexane, 0.7 mL/min, 30 °C, 220 nm; t_{R1} = 8.11 min, t_{R2} = 12.69 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.106	BB	0.1807	1353.62769	115.51038	53.6074
2	12.689	BB	0.3123	1171.44958	57.83095	46.3926

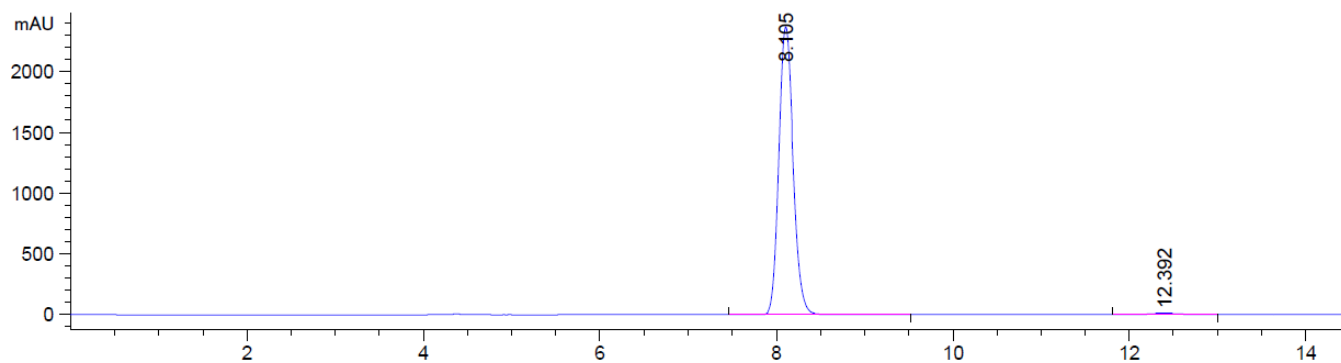
Procedure for Optical Resolution of (\pm)-DHTP by Enantiopure (*R*)-3



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To a solution of (\pm)-1,16-dihydroxytetraphenylene (**DHTP**) (168 mg, 0.5 mmol) and Cs_2CO_3 (342 mg, 2.1 eq.) in CH_2Cl_2 (10 mL) was added enantiopure oxazoline-based cyclometalated gold(III) dichloride (**(R)-3**) (252 mg, 1.0 eq.). A yellow precipitate was formed in a suspension quickly (within minutes). The resulting mixture was stirred for additional 1 h at room temperature (25 °C). The yellow precipitate was collected by filtration, washed with H_2O (5 mL \times 2) and CH_2Cl_2 (5 mL \times 2), dried under vacuum to give *O,O'*-chelated **DHTP/Au(III)** complexes (**(S,R)-4**) as a yellow powder. Subsequently, the obtained (**(S,R)-4**) was added in CH_2Cl_2 (10 mL). To the resulting suspension of (**(S,R)-4**) in CH_2Cl_2 was added 6N hydrochloric acid (2 mL) at room temperature. After being stirred for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (100% CH_2Cl_2 to EtOAc/hexane 1:1) to give (**(S)-DHTP**) as a white solid (74 mg, 44% yield, 99% *ee*), and recovered (**(R)-3**) (108 mg, 43% yield).

HPLC spectrum of the obtained (**(S)-DHTP**): Daicel Chiralpak[®] AD-H, 40% *i*PrOH, 60% hexane, 0.7 mL/min, 30 °C, 220 nm; 99% *ee* (t_{R} (major) = **8.10 min**, t_{R} (minor) = 12.39 min).



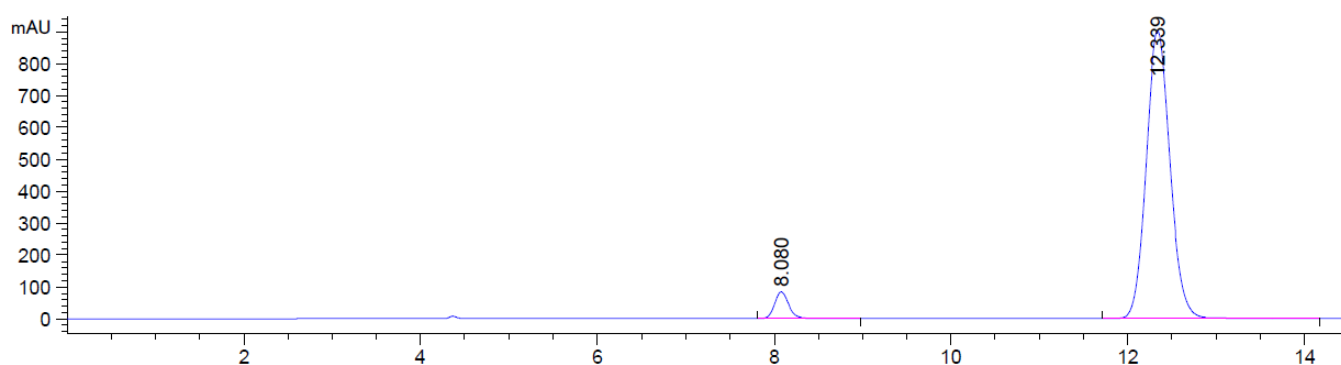
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.105	BB	0.1749	2.65666e4	2367.14819	99.2822
2	12.392	BB	0.2897	192.07320	10.19740	0.7178

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The filtrate [~ 20 mL DCM, mainly containing (*R,R*)-**4**] was washed with H₂O (10 mL \times 2) and the CH₂Cl₂ layer was separated. To the collected CH₂Cl₂ layer was added 6N hydrochloric acid (2 mL) at room temperature. After being stirred for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (100% CH₂Cl₂ to EtOAc/hexane 1:1) to give (*R*)-**DHTP** as a white solid (83 mg, 49% yield, 90% *ee*), and recovered (*R*)-**3** (127 mg, 51% yield).

HPLC spectrum of the obtained (*R*)-**DHTP**: Daicel Chiralpak[®] AD-H, 40% *i*PrOH, 60% hexane, 0.7 mL/min, 30 °C, 220 nm; 90% *ee* (**t_R (major) = 12.34 min**, t_R (minor) = 8.08 min).

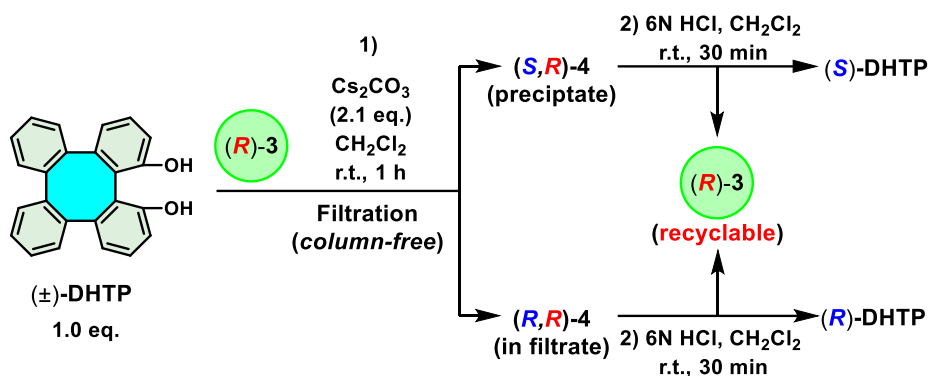


Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.080	BB	0.1659	899.11420	83.29595	5.0858
2	12.339	BB	0.2871	1.67796e4	901.87585	94.9142

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HPLC Spectra of (*S*)-DHTP and (*R*)-DHTP from Multi-Grams Scale Optical Resolution of (\pm)-DHTP and Recyclability Experiments of (*R*)-**3**^{[a][b][c]}



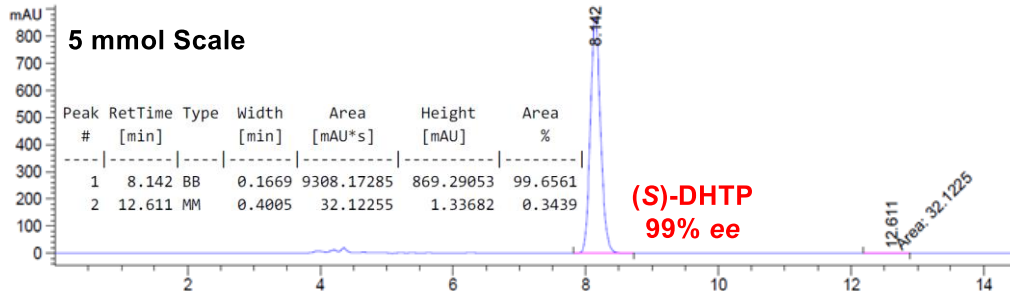
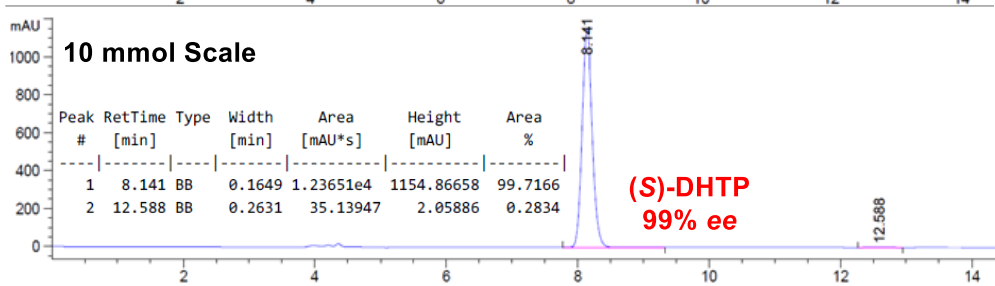
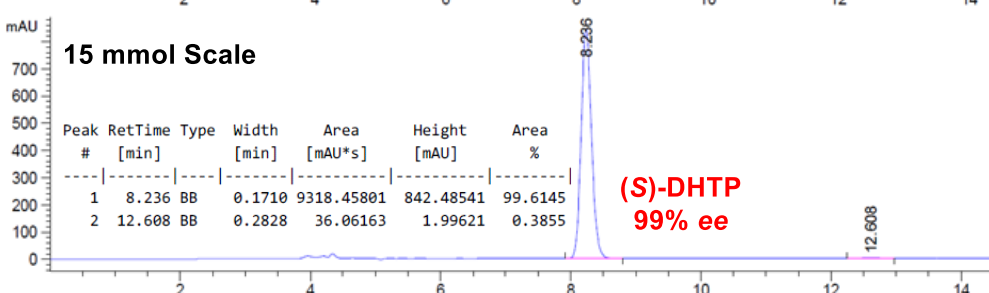
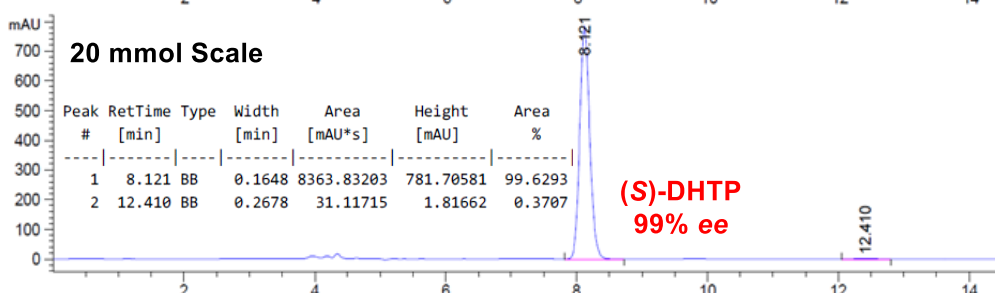
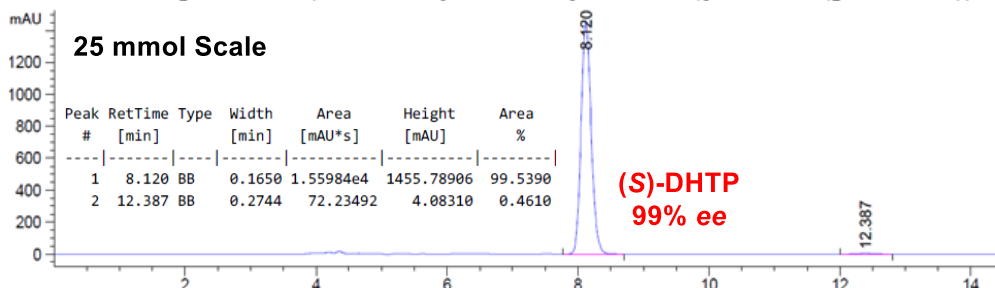
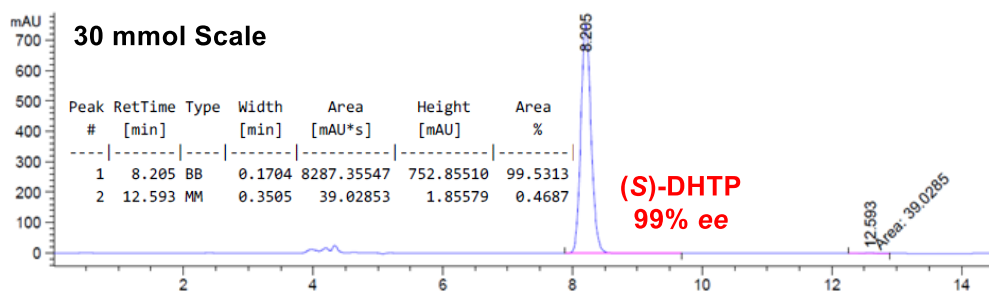
Entry	Scale of (\pm)-DHTP (mmol)	Yield and <i>ee</i> of (<i>S</i>)-DHTP	Yield and <i>ee</i> of (<i>R</i>)-DHTP	Recovery yield of (<i>R</i>)- 3 (%)
		Yield [<i>ee</i>] (%)	Yield [<i>ee</i>] (%)	
1	30	45 [99]	49 [88]	98 (14.8 g)
2 ^[d]	25	47 [99]	50 [95]	99
3 ^[d]	20	45 [99]	50 [89]	98
4 ^[d]	15	46 [99]	49 [93]	98
5 ^[d]	10	46 [99]	48 [96]	99
6 ^[d]	5	48 [99]	50 [87]	98

[a] Reaction conditions: step 1): (\pm)-DHTP (1.0 eq.), (*R*)-**3** (1.0 eq.), Cs_2CO_3 (2.1 eq.), CH_2Cl_2 ([substrate] = 0.1 M), room temperature (25 °C), reaction time: 1 h; step 2): CH_2Cl_2 ([substrate] = 0.1 M), HCl (6 N, aq.), room temperature, reaction time: 30 min. [b] Yield of isolated product. [c] *ee*% was determined by chiral HPLC analysis. [d] (*R*)-**3** came from the last reaction cycle.

HPLC analyses conditions: Daicel Chiralpak[®] AD-H, 40% *i*PrOH, 60% hexane, 0.7 mL/min, 30 °C, 220 nm.

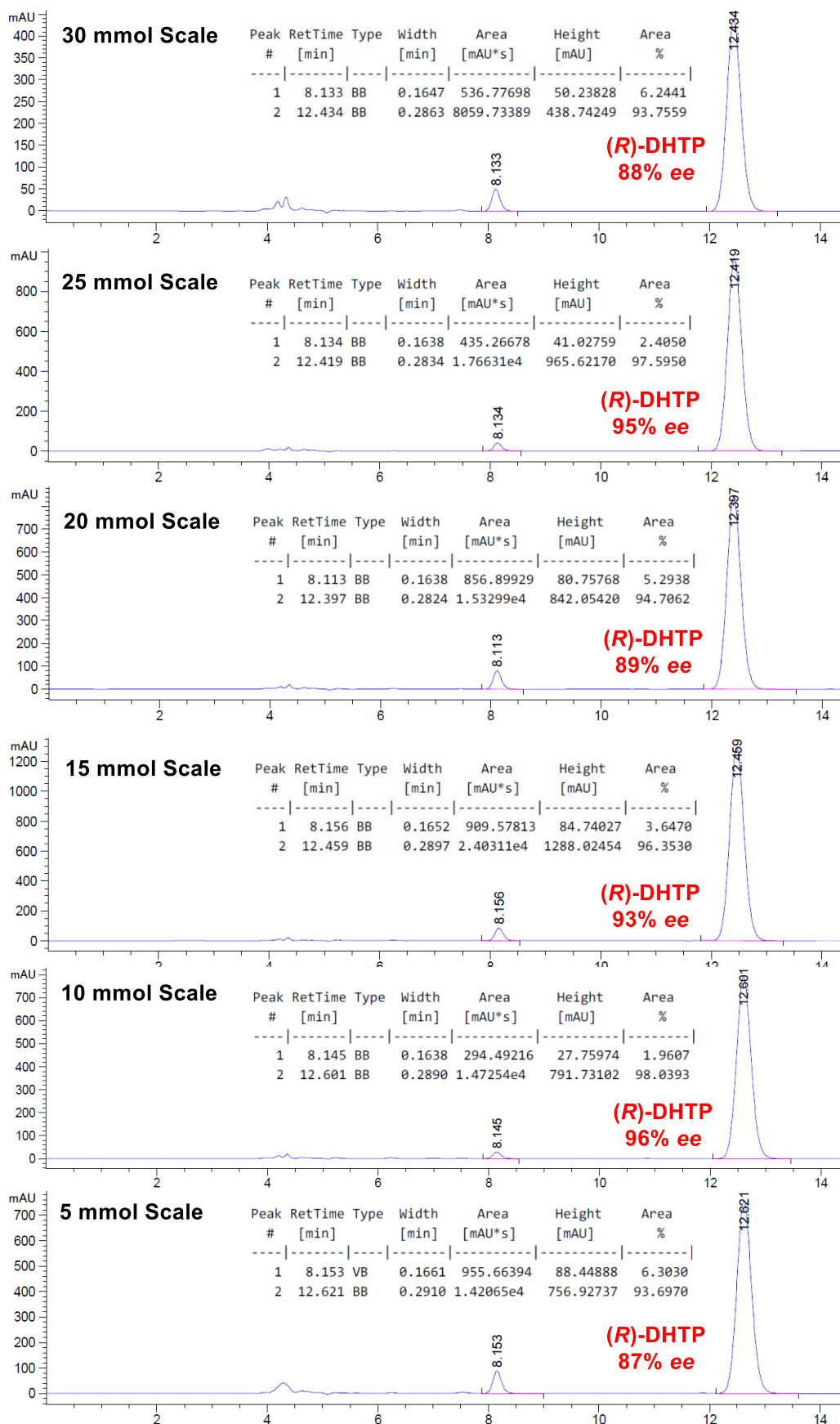
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A) HPLC Spectra of the Obtained (S)-DHTP from Different Scales



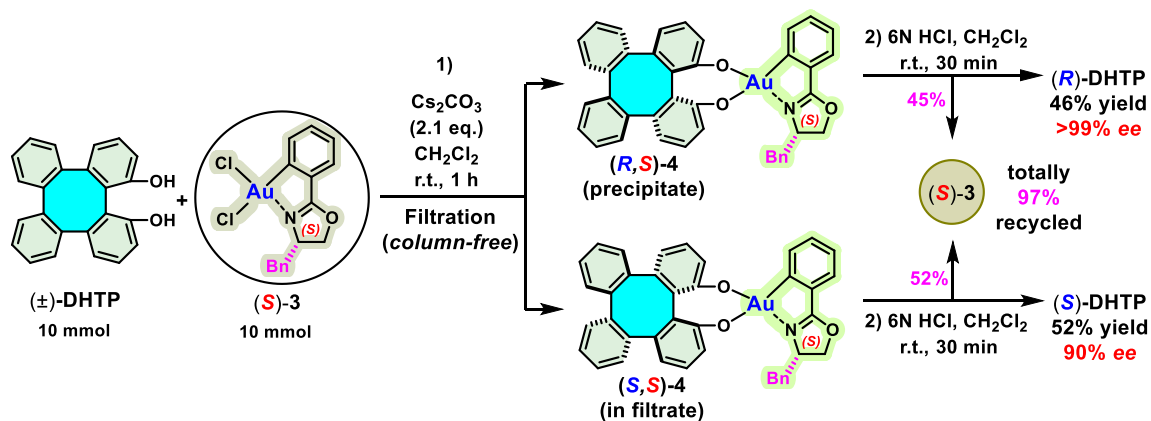
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B) HPLC Spectra of the Obtained (*R*)-DHTP from Different Scales



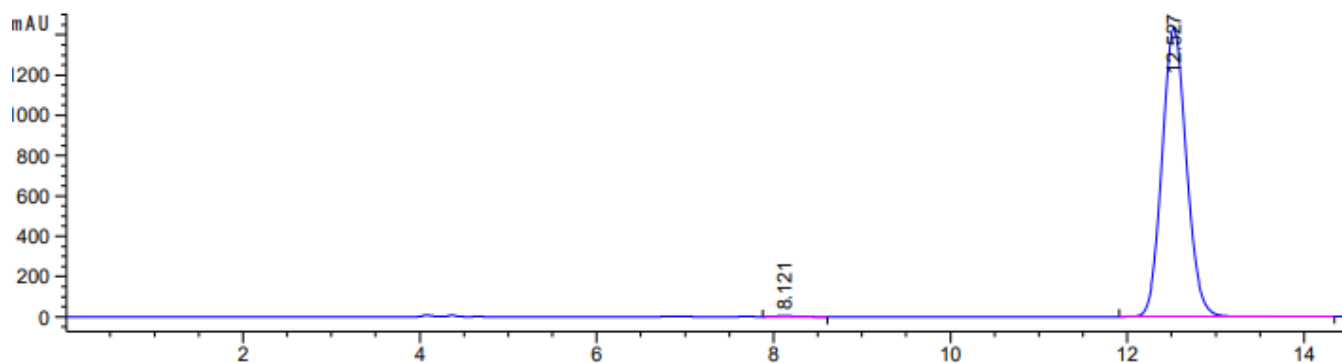
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Procedure for Optical Resolution of (\pm)-DHTP by Enantiopure (*S*)-3



To a solution of (\pm)-**DHTP** (3.36 g, 10 mmol) and Cs_2CO_3 (6.83 g, 2.1 eq.) in CH_2Cl_2 (100 mL) was added enantiopure oxazoline-based cyclometalated gold(III) dichloride (*S*)-**3** (5.04 g, 10 mmol). A yellow precipitate was formed in a suspension quickly (within minutes). The resulting mixture was stirred for additional 1 h at room temperature (25 °C). The yellow precipitate was collected by filtration, washed with H_2O (100 mL \times 2) and CH_2Cl_2 (100 mL \times 2), dried under vacuum to give *O,O'*-chelated **DHTP**/Au(III) complexes (*R,S*)-**4** as a yellow powder. Subsequently, the obtained (*R,S*)-**4** was added in CH_2Cl_2 (50 mL). To the resulting suspension of (*R,S*)-**4** in CH_2Cl_2 was added 6N hydrochloric acid (10 mL) at room temperature. After being stirred for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (100% CH_2Cl_2 to EtOAc/hexane 1:1) to give (*R*)-**DHTP** as a white solid (1.55 g, 46% yield, >99% *ee*), and recovered (*S*)-**3** (2.26 g, 45% yield).

HPLC spectrum of the obtained (*R*)-**DHTP**: Daicel Chiralpak[®] AD-H, 40% *i*PrOH, 60% hexane, 0.7 mL/min, 30 °C, 220 nm; >99% *ee* (t_{R} (major) = 12.53 min, t_{R} (minor) = 8.12 min).



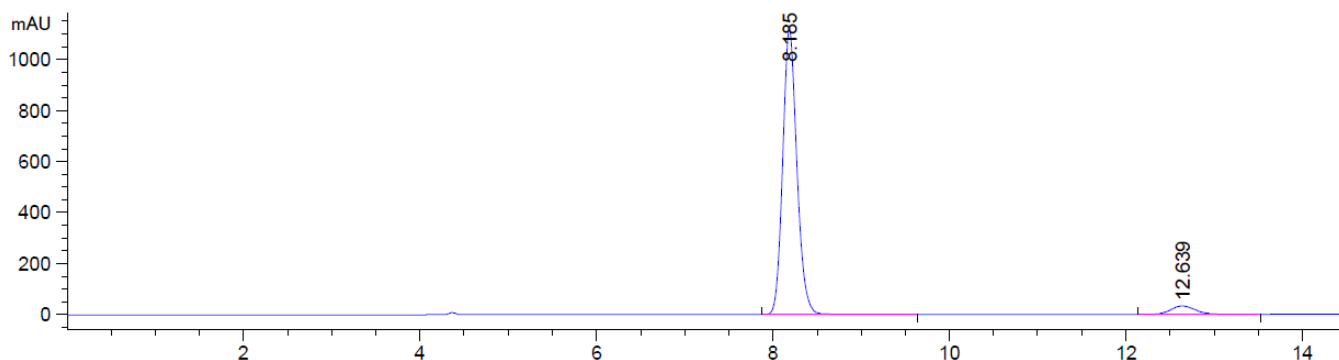
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Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.121	BB	0.1711	66.52022	5.91744	0.2408
2	12.527	BB	0.2980	2.75638e4	1435.65161	99.7592

The filtrate [\sim 300 mL CH_2Cl_2 , mainly containing (*S,S*)-**4**] was washed with H_2O (100 mL \times 2) and the CH_2Cl_2 layer was separated. To the collected CH_2Cl_2 layer was added 6N hydrochloric acid (10 mL) at room temperature. After being stirred for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (100% CH_2Cl_2 to EtOAc/hexane 1:1) to give (*S*)-**DHTP** as a white solid (1.74 g, 52% yield, 90% *ee*), and recovered (*S*)-**3** (2.61 g, 52% yield).

HPLC spectrum of the obtained (*S*)-**DHTP**: Daicel Chiralpak[®] AD-H, 40% *i*PrOH, 60% hexane, 0.7 mL/min, 30 °C, 220 nm; 90% *ee* (t_{R} (major) = **8.18 min**, t_{R} (minor) = 12.64 min).

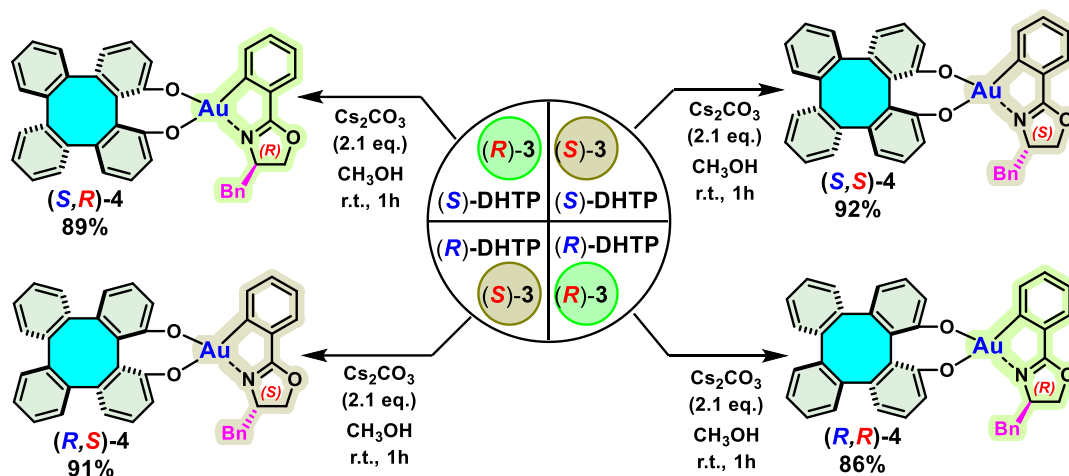


Signal 2: DAD1 B, Sig=220,4 Ref=off

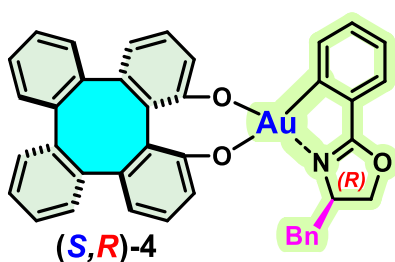
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.185	BB	0.1727	1.26352e4	1128.18079	95.1578
2	12.639	BB	0.3024	642.95929	32.84866	4.8422

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General Procedure for Synthesis of Enantiopure DHTP/oxazoline Au(III) Complexes



To a solution of enantiopure (*S*)-DHTP or (*R*)-DHTP (34.0 mg, 0.1 mmol) and Cs_2CO_3 (68.3 mg, 0.21 mmol) in CH_3OH (2.0 mL) was added enantiopure oxazoline-based cyclometalated gold(III) dichloride (*R*)-3 or (*S*)-3 (50.4 mg, 0.1 mmol) at room temperature (25 °C). A yellow precipitate was formed in a suspension quickly (within minutes). The mixture was stirred for additional 1 h at room temperature, and then the precipitate was collected by filtration, washed by H_2O and CH_3OH , dried under vacuum to give the corresponding *O,O'*-chelated DHTP/oxazoline Au(III) complexes (*S,R*)-4, (*R,S*)-4, (*S,S*)-4 and (*R,R*)-4, respectively.



Yellow solid. 68.0 mg, 89% yield. mp 236.7 – 237.2 °C. $[\alpha]^{20}_{\text{D}}$: –979.7 ($c = 1.06$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$) δ 7.75 (d, $J = 7.7$ Hz, 1H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.46 – 7.40 (m, 2H), 7.34 – 7.23 (m, 8H), 7.23 – 7.19 (m, 1H), 7.15 (q, $J = 2.5$ Hz, 2H), 7.12 – 7.07 (m, 2H), 7.06 – 6.99 (m, 3H), 6.88 (d, $J = 7.9$ Hz, 1H), 6.73 (d, $J = 6.5$ Hz, 1H), 6.50 (d, $J = 7.5$ Hz, 1H), 5.09 (t, $J = 8.7$ Hz, 1H), 4.93 – 4.84 (m, 2H), 3.56 (d, $J = 13.4$ Hz, 1H), 3.04 (dd, $J = 13.6, 8.9$ Hz, 1H).

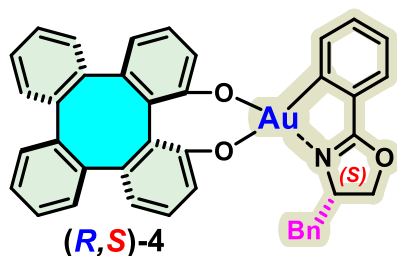
$^{13}\text{C NMR}$ (150 MHz, $\text{DMSO}-d_6$) δ 180.32, 161.08, 160.10, 144.31, 143.53, 142.72, 142.56, 142.30, 141.66, 141.34, 136.47, 134.58, 134.03, 131.81, 129.85, 129.17, 129.09, 129.06, 128.88, 128.59, 128.16,

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128.13, 128.08, 127.66, 127.58, 127.56, 127.42, 127.36, 124.09, 121.86, 121.70, 120.77, 77.82, 62.43, 38.02.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{40}H_{29}O_3NAu]^+$ 768.1807, found 768.1809.

IR (neat): 3058, 3027, 2923, 2852, 1620, 1579, 1560, 1491, 1430, 1306, 1265, 1243, 907, 731 cm^{-1} .



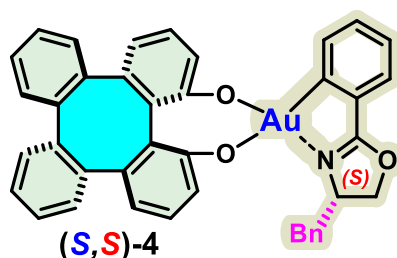
Yellow solid. 70.0 mg, 91% yield. mp 228.9 – 230.4 °C. $[\alpha]_D^{20}$: +924.0 ($c = 1.0$, $CHCl_3$).

1H NMR (600 MHz, $DMSO-d_6$) δ 7.75 (d, $J = 7.8$ Hz, 1H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.46 – 7.40 (m, 2H), 7.33 – 7.24 (m, 8H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.15 (d, $J = 6.3$ Hz, 2H), 7.10 (t, $J = 8.3$ Hz, 2H), 7.06 – 7.00 (m, 3H), 6.88 (d, $J = 7.9$ Hz, 1H), 6.73 (d, $J = 6.3$ Hz, 1H), 6.50 (d, $J = 7.5$ Hz, 1H), 5.09 (t, $J = 8.8$ Hz, 1H), 4.93 – 4.84 (m, 2H), 3.56 (d, $J = 12.3$ Hz, 1H), 3.03 (dd, $J = 13.6, 8.9$ Hz, 1H).

^{13}C NMR (150 MHz, $DMSO-d_6$) δ 180.31, 161.08, 160.10, 144.31, 143.53, 142.72, 142.56, 142.30, 141.66, 141.34, 136.47, 134.58, 134.03, 131.81, 129.85, 129.17, 129.10, 129.06, 128.88, 128.59, 128.16, 128.13, 128.08, 127.66, 127.58, 127.55, 127.42, 127.36, 124.09, 121.86, 121.70, 120.77, 77.82, 62.43, 38.02.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{40}H_{29}O_3NAu]^+$ 768.1807, found 768.1808.

IR (neat): 3055, 3026, 2925, 2852, 1619, 1578, 1560, 1490, 1430, 1306, 1266, 1243, 910, 733 cm^{-1} .



Yellow solid. 71.0 mg, 92% yield. mp 235.9 – 236.5 °C. $[\alpha]_D^{20}$: –658.2 ($c = 1.0$, $CHCl_3$).

1H NMR (600 MHz, CD_2Cl_2) δ 7.95 (d, $J = 7.8$ Hz, 1H), 7.54 (td, $J = 7.6, 1.6$ Hz, 1H), 7.40 – 7.22 (m, 13H), 7.18 (dd, $J = 5.6, 3.3$ Hz, 1H), 7.16 (td, $J = 8.3, 1.8$ Hz, 2H), 7.05 (dt, $J = 14.0, 7.7$ Hz, 2H), 6.98 (dd, $J = 8.1, 1.3$ Hz, 1H), 6.86 (dd, $J = 7.6, 1.3$ Hz, 1H), 6.63 (dd, $J = 7.4, 1.3$ Hz, 1H), 4.84 – 4.72 (m, 3H), 3.76 (dd, $J = 13.8, 2.9$ Hz, 1H), 3.33 (dd, $J = 13.8, 7.0$ Hz, 1H).

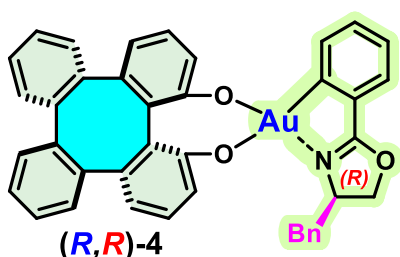
SUPPORTING INFORMATION

^{13}C NMR (150 MHz, CD_2Cl_2) δ 181.20, 160.55, 144.93, 144.09, 143.68, 143.12, 142.48, 142.26, 141.76, 135.48, 134.82, 134.57, 132.43, 130.36, 129.53, 129.51, 129.20, 129.07, 129.00, 128.70, 128.39, 128.36, 128.00, 127.87, 127.67, 127.64, 127.41, 127.38, 124.84, 122.28, 121.35, 121.27, 76.90, 62.68, 39.38.

DEPT135 ^{13}C NMR (150 MHz, CD_2Cl_2) δ 134.27, 129.82, 128.99, 128.96, 128.66, 128.53, 128.45, 128.16, 127.85, 127.81, 127.45, 127.33, 127.12, 127.09, 126.86, 124.30, 121.74, 120.81, 120.72, 76.35(CH_2), 62.13, 38.83(CH_2).

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{40}\text{H}_{29}\text{O}_3\text{NAu}]^+$ 768.1807, found 768.1807.

IR (neat): 3056, 3024, 2923, 2855, 1619, 1579, 1560, 1491, 1430, 1305, 1265, 1241, 908, 732 cm^{-1} .



Yellow solid. 66.0 mg, 86% yield. mp 236.0 – 236.7 °C. $[\alpha]^{20}_{\text{D}}$: +693.1 ($c = 1.02$, CHCl_3).

^1H NMR (400 MHz, CD_2Cl_2) δ 8.00 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.58 (td, $J = 7.6, 1.7$ Hz, 1H), 7.44 – 7.27 (m, 13H), 7.25 – 7.18 (m, 3H), 7.10 (dt, $J = 8.4, 7.5$ Hz, 2H), 7.03 (dd, $J = 8.0, 1.5$ Hz, 1H), 6.91 (dd, $J = 7.5, 1.3$ Hz, 1H), 6.69 (dd, $J = 7.3, 1.4$ Hz, 1H), 4.91 – 4.70 (m, 3H), 3.79 (dd, $J = 13.9, 2.5$ Hz, 1H), 3.46 – 3.30 (m, 1H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 180.65, 160.01, 159.98, 144.40, 143.58, 143.11, 142.57, 141.95, 141.73, 141.23, 134.93, 134.29, 134.01, 131.90, 129.84, 129.00, 128.96, 128.68, 128.55, 128.48, 128.19, 127.88, 127.85, 127.48, 127.34, 127.15, 127.12, 126.89, 126.83, 124.32, 121.76, 120.86, 120.74, 76.34, 62.12, 38.82.

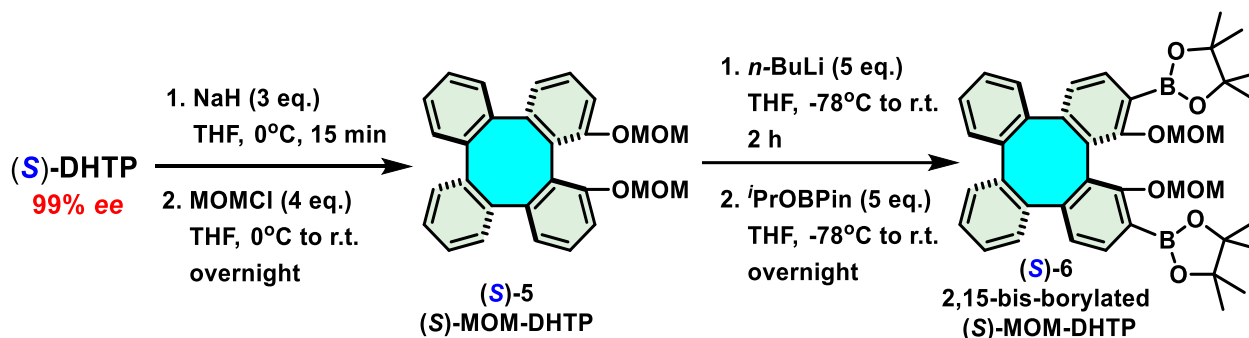
DEPT135 ^{13}C NMR (100 MHz, CD_2Cl_2) δ 134.29, 129.84, 129.00, 128.96, 128.68, 128.55, 128.48, 128.19, 127.88, 127.85, 127.48, 127.34, 127.15, 127.12, 126.90, 124.32, 121.77, 120.86, 120.74, 76.34, 62.12, 38.82.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{40}\text{H}_{29}\text{O}_3\text{NAu}]^+$ 768.1807, found 768.1809.

IR (neat): 3058, 3024, 2928, 2855, 1618, 1578, 1559, 1491, 1430, 1305, 1266, 1242, 908, 731 cm^{-1} .

SUPPORTING INFORMATION

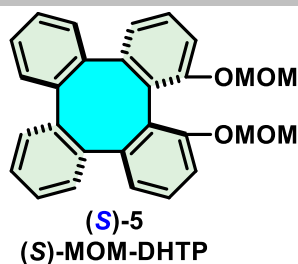
Procedure for Methoxymethylation and Borylation of (*S*)-DHTP



To a suspension of NaH (60% in mineral oil, 2.4 g, 60 mmol) in dry THF (150 mL), enantiopure (*S*)-**DHTP** (6.72 g, 20 mmol) was added under Argon atmosphere at 0 °C. After being stirred for 15 min, chloromethyl methyl ether (6.1 mL, 80 mmol) was added dropwise. The resulting mixture was slowly warmed to room temperature (25 °C) and stirred overnight. The reaction was quenched with ice water (100 mL), and then THF was removed by evaporation. The residual aqueous layer was extracted with CH₂Cl₂ (150 mL × 3). The combined organic phase was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH₂Cl₂/EtOAc/hexane 1:1:10) to give 1,16-*bis*(methoxymethoxy)tetraphenylene [(*S*)-**5**] as a white solid (8.06 g, 95% yield).

To a solution of (*S*)-**5** (8.48 g, 20 mmol) in dry THF (350 mL) was added 1.6 M *n*-BuLi in hexane (62.5 mL, 100 mmol, 5 eq.). The solution was stirred for 2 h at room temperature (25 °C). The resulting suspension was cooled to -78 °C, and 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxabrolane (20.4 mL, 100 mmol) was added *via* syringe over a period of 20 min. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was cooled to 0 °C, H₂O (150 mL) was added, and the reaction mixture was stirred for 1 h. The THF was removed by evaporation. The residual aqueous layer was extracted with CH₂Cl₂ (200 mL × 3). The combined organic phase was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH₂Cl₂/EtOAc/hexane 1:1:6) to give (*S*)-**6** as white solid (12.17 g, 90% yield).

SUPPORTING INFORMATION



White solid. 8.06 g, 95% yield.

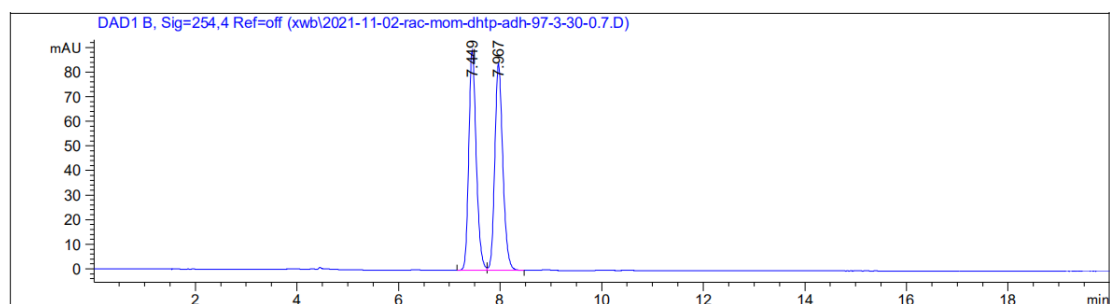
$^1\text{H NMR}$ (600 MHz, CD_2Cl_2) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 5.07 (d, J = 6.6 Hz, 1H), 4.96 (d, J = 6.5 Hz, 1H), 3.31 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CD_2Cl_2) δ 154.41, 143.40, 141.45, 141.36, 128.96, 128.23, 128.04, 127.33, 127.29, 127.15, 122.87, 114.09, 95.19, 55.60.

HRMS (ESI): $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{28}\text{H}_{24}\text{NaO}_4]^+$ 447.1567, found 447.1568.

HPLC: Daicel Chiralpak[®] AD-H, 3% i PrOH, 97% hexane, 0.7 mL/min, 30 °C, 254 nm; >99% *ee* (t_R (major) = 8.25 min).

Racemic

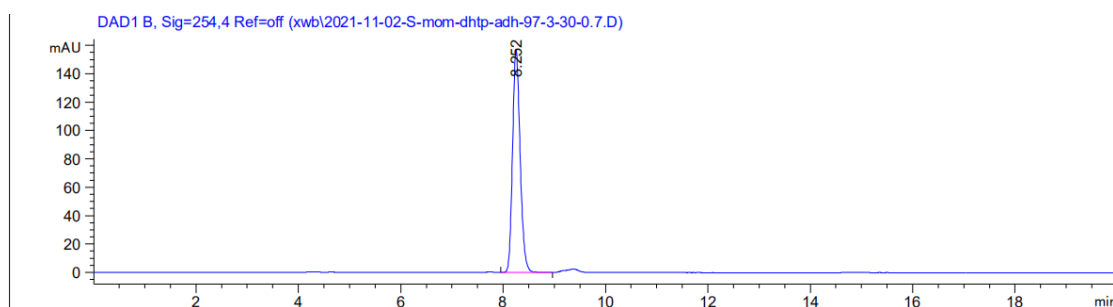


Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.449	BV	0.1575	914.72015	89.31101	49.9080
2	7.967	VB	0.1675	918.09406	84.01053	50.0920

Totals : 1832.81421 173.32154

Enantioenriched

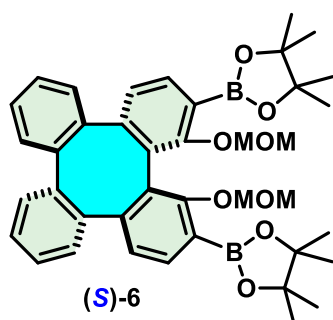


SUPPORTING INFORMATION

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.252	BB	0.1579	1611.13196	156.79631	100.0000

Totals : 1611.13196 156.79631



White solid. 12.17 g, 90% yield. mp 110.5 – 111.2 °C. $[\alpha]_D^{25}$: -17.1 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CD_2Cl_2) δ 7.69 (d, $J = 7.6$ Hz, 1H), 7.37 – 7.33 (m, 2H), 7.28 – 7.25 (m, 1H), 7.20 – 7.17 (m, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 4.83 (d, $J = 6.0$ Hz, 1H), 4.53 (d, $J = 6.0$ Hz, 1H), 2.84 (s, 3H), 1.36 (s, 6H), 1.36 (s, 6H).

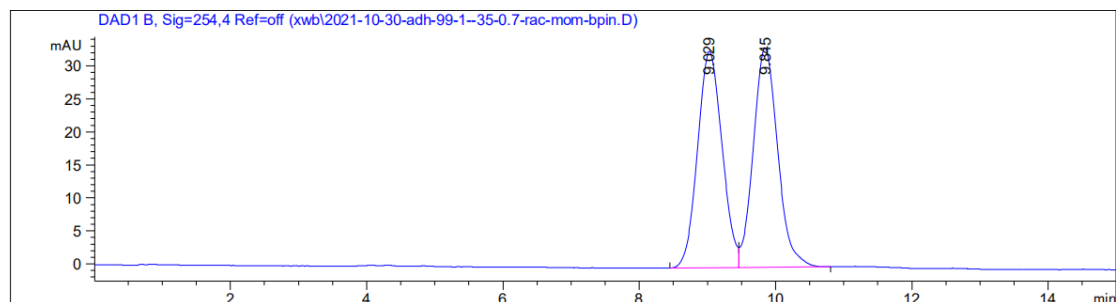
$^{13}\text{C NMR}$ (150 MHz, CD_2Cl_2) δ 160.62, 146.76, 141.32, 141.16, 135.84, 131.44, 129.05, 128.59, 127.48, 127.25, 124.69, 100.66, 83.59, 55.96, 24.62, 24.53.

HRMS (ESI): $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{40}\text{H}_{46}\text{B}_2\text{O}_8\text{Na}]^+$ 699.3271, found 699.3278.

IR (neat): 3063, 2979, 2928, 2823, 1595, 1467, 1360, 1308, 1218, 1140, 1063, 968, 858, 762, 667 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 1% i PrOH, 99% hexane, 0.7 mL/min, 35 °C, 254 nm; >99% *ee* (t_R (major) = 9.78 min).

Racemic

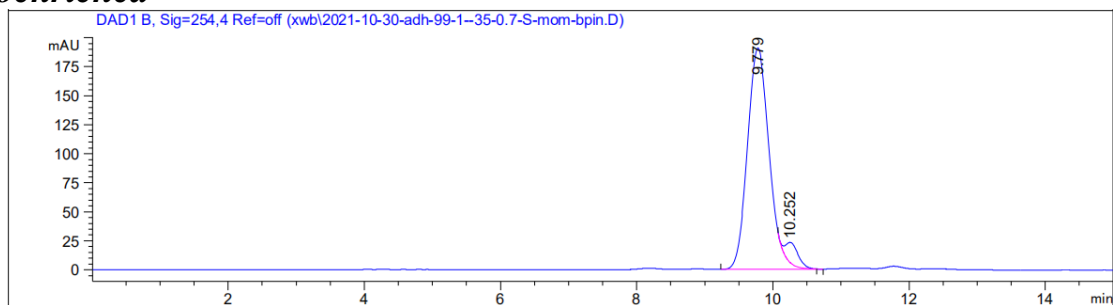


SUPPORTING INFORMATION

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.029	BV	0.3858	820.03979	32.78717	49.7838
2	9.845	VB	0.3861	827.16260	33.26366	50.2162
Totals :				1647.20239	66.05083	

Enantioenriched



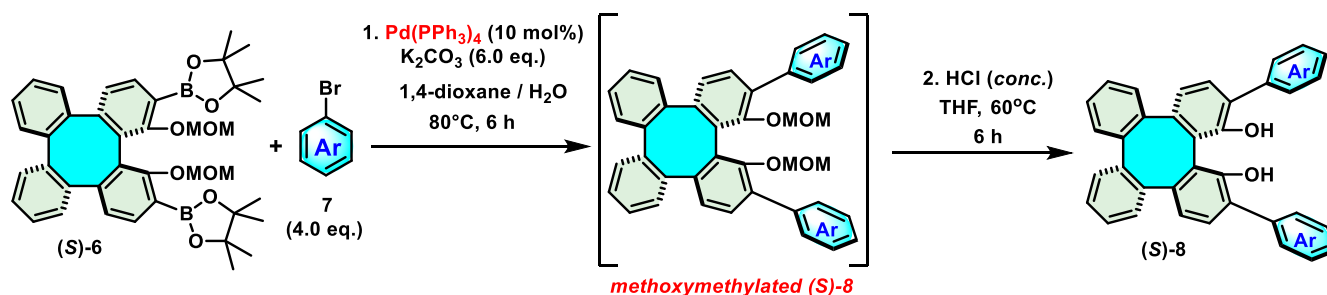
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.779	BV R	0.3445	4225.39648	190.69658	94.7313
2	10.252	VB E	0.2028	235.00377	17.26702	5.2687
Totals :				4460.40025	207.96360	

SUPPORTING INFORMATION

General Procedure for Synthesis of 2,15-diaryl DHTPs

1) Standard Procedure:

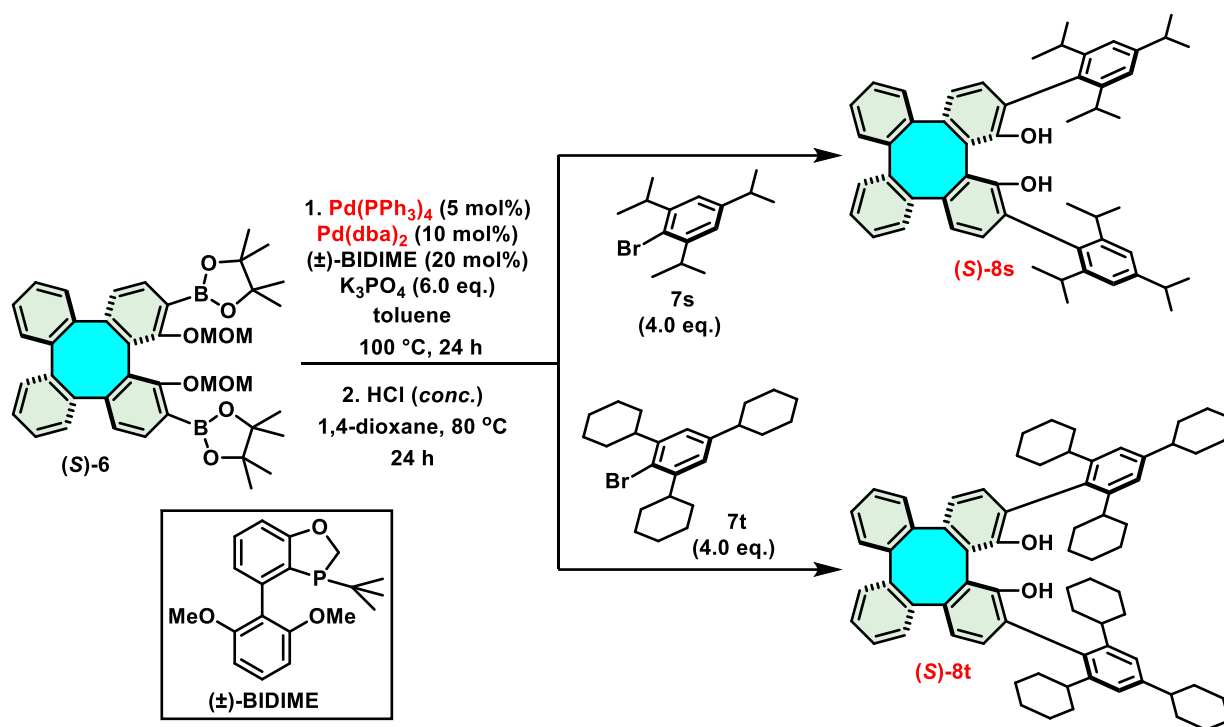


To a Schlenk flask were added (S)-6 (1 mmol, 1.0 eq.), aryl bromine 7 (4.0 eq.), $\text{Pd}(\text{PPh}_3)_4$ (10 mol%), K_2CO_3 (6.0 eq.), 1,4-dioxane (16 mL) and H_2O (4 mL). The mixture was degassed and refilled with Ar three times. The mixture was heated at 80°C for 6 h. After cooling to room temperature (25°C), the mixture was diluted with H_2O (30 ml), and the aqueous layer was extracted with CH_2Cl_2 ($50\text{ mL} \times 3$). The combined organic phase was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2 /hexane or EtOAc/hexane) to give the corresponding precursor, methoxymethylated (S)-8.

The obtained methoxymethylated (S)-8 was dissolved in THF (10 mL) followed by the addition of concentrated HCl (37% w/w, 2 mL). The mixture was heated at 60°C for 6 h (or 24 h). The solvents were removed under reduced pressure, and the resulting residue was dissolved in CH_2Cl_2 . This organic phase was washed with saturated aqueous NaHCO_3 , and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane or EtOAc/hexane) to give the corresponding 2,15-diaryl DHTP (S)-8.

SUPPORTING INFORMATION

2) Modified Procedure [for (S)-8s and (S)-8t]:

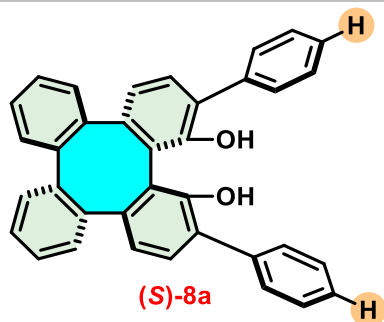


To a Schlenk flask were added (S)-6 (1 mmol, 1.0 eq.), aryl bromine **7** (4.0 eq.), Pd(PPh₃)₄ (5 mol%), Pd(dba)₂ (10 mol%), (±)-BIDIME (20 mol%), K₃PO₄ (6.0 eq.), dry toluene (20 mL). The mixture was degassed and refilled with Ar three times. The mixture was heated at 100 °C for 24 h. After cooling to room temperature (25 °C), the mixture was diluted with H₂O (30 ml), and the aqueous layer was extracted with CH₂Cl₂ (50 mL × 3). The combined organic phase was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH₂Cl₂/hexane) to give the corresponding precursor, *methoxymethylated* (S)-8.

The obtained methoxymethylated (S)-8 was dissolved in 1,4-dioxane (10 mL) followed by the addition of concentrated HCl (37% w/w, 2 mL). The mixture was heated at 80 °C for 24 h. The solvents were removed under reduced pressure, and the resulting residue was dissolved in CH₂Cl₂. This organic phase was washed with saturated aqueous NaHCO₃, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/hexane) to give the corresponding 2,15-diaryl **DHTP** (S)-8.

Compounds (±)-8 for HPLC determination were prepared by using racemic (±)-6 to instead of (S)-6 under the above standard conditions and modified conditions.

SUPPORTING INFORMATION



White solid. 439.6 mg, 90% yield. mp 150.0 – 151.5 °C. $[\alpha]_D^{25}$: +190.2 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 (d, $J = 7.2$ Hz, 2H), 7.40 (t, $J = 7.7$ Hz, 2H), 7.34 – 7.29 (m, 4H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.19 – 7.15 (m, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 5.27 (s, 1H).

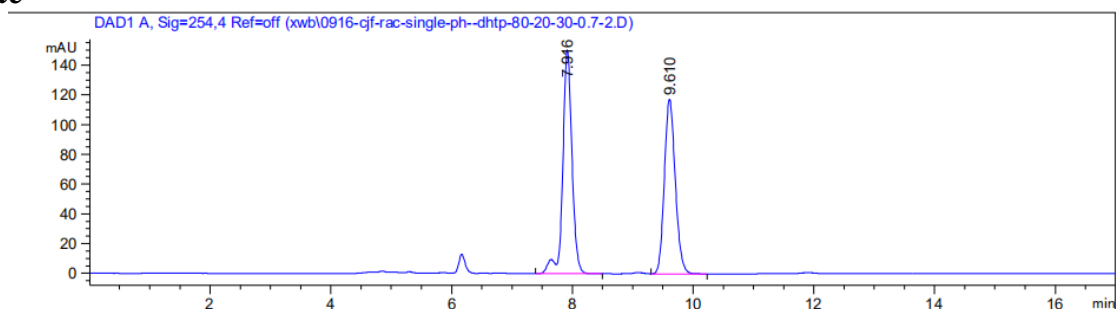
$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.16, 143.74, 141.44, 141.01, 137.30, 130.48, 129.34, 129.28, 128.62, 128.19, 127.58, 127.50, 127.41, 127.30, 122.20, 121.74.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{36}\text{H}_{25}\text{O}_2]^+$ 489.1850, found 489.1850.

IR (neat): 3532, 3058, 3019, 2925, 2852, 1467, 1417, 1219, 1183, 906, 751, 700 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 20% *i*PrOH, 80% hexane, 0.7 mL/min, 30 °C, 254 nm; 99% *ee* (t_{R} (major) = 9.64 min, t_{R} (minor) = 8.04 min).

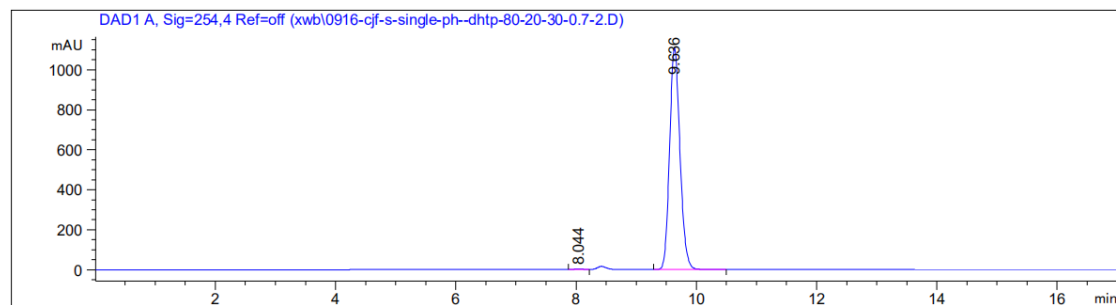
Racemic



Signal 1: DAD1 A, Sig=254,4 Ref=off

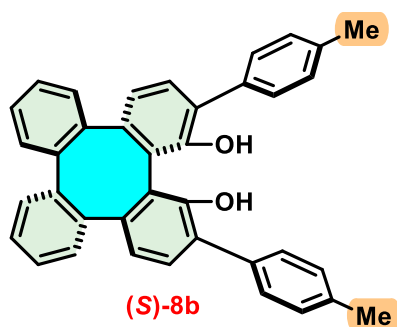
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.916	VB R	0.1542	1604.34961	150.30582	52.0873
2	9.610	VB	0.1947	1475.76526	117.40374	47.9127

Enantioenriched



SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.044	BV	0.1462	31.53606	3.33837	0.2369
2	9.636	BB	0.1856	1.32782e4	1109.50366	99.7631



White solid. 418.6 mg, 81% yield. mp 147.7 – 149.8 °C. $[\alpha]_D^{25}$: +194.7 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.39 (d, $J = 8.0$ Hz, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.19 (m, 3H), 7.18 – 7.14 (m, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 5.27 (s, 1H), 2.35 (s, 3H).

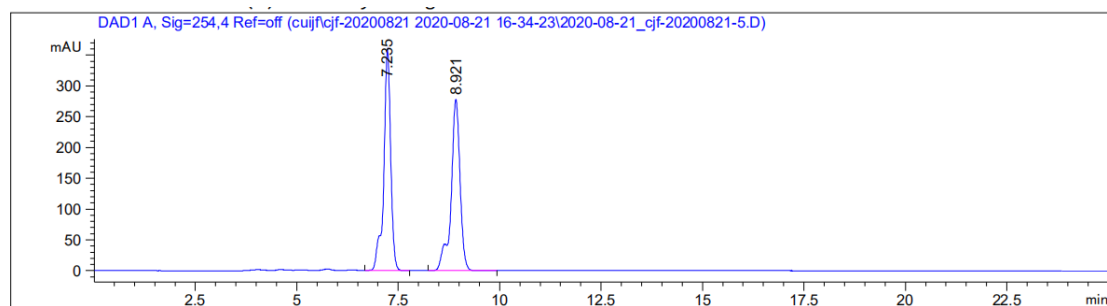
$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.21, 143.49, 141.50, 141.14, 137.28, 134.35, 130.34, 129.39, 129.33, 129.15, 128.25, 127.54, 127.40, 127.28, 122.15, 121.83, 21.23.

HRMS (ESI): $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{38}\text{H}_{28}\text{O}_2\text{Na}]^+$ 539.1982, found 539.1987.

IR (neat): 3531, 3058, 3019, 2917, 2857, 1468, 1429, 1387, 1184, 906, 815, 750 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 20% *i*PrOH, 80% hexane, 0.7 mL/min, 30 °C, 254 nm; 99% *ee* (t_R (major) = 9.01 min, t_R (minor) = 7.33 min).

Racemic



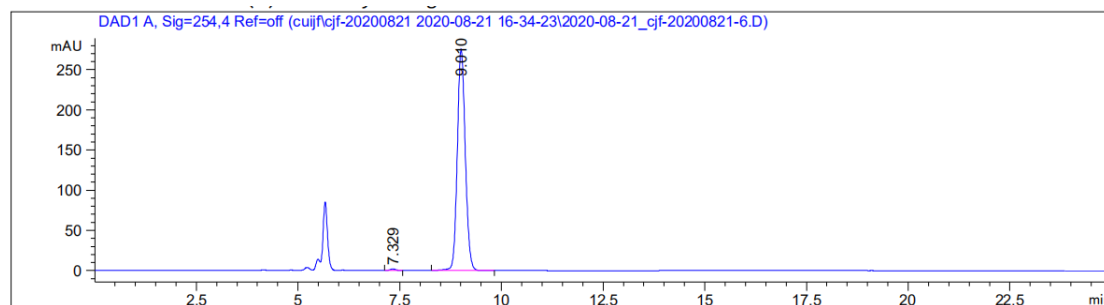
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.235	VB R	0.1781	4301.55078	358.21835	49.9712
2	8.921	VB R	0.2198	4306.51709	277.80750	50.0288

Totals : 8608.06787 636.02585

SUPPORTING INFORMATION

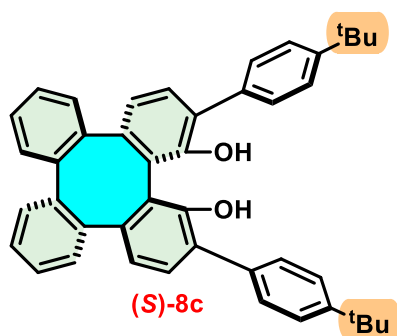
Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.329	BB	0.1579	19.59820	1.93942	0.5170
2	9.010	BB	0.2116	3771.25586	275.60733	99.4830

Totals : 3790.85406 277.54675



White solid. 510.8 mg, 85% yield. mp 151.2 – 153.6 °C. $[\alpha]_D^{25}$: +195.9 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.47 – 7.39 (m, 4H), 7.32 – 7.27 (m, 3H), 7.25 (d, $J = 7.8$ Hz, 1H), 7.15 (ddd, $J = 4.7, 3.2, 1.5$ Hz, 1H), 6.87 (d, $J = 7.9$ Hz, 1H), 5.28 (s, 1H), 1.33 (s, 9H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 150.44, 149.25, 143.51, 141.51, 141.14, 134.32, 130.38, 129.33, 128.94, 128.23, 127.54, 127.40, 127.17, 125.62, 122.16, 121.76, 34.63, 31.39.

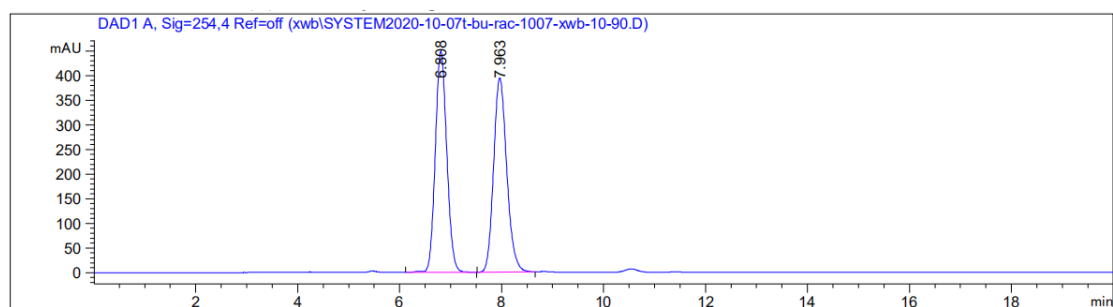
HRMS (ESI): $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{44}\text{H}_{40}\text{O}_2\text{Na}]^+$ 623.2921, found 623.2921.

IR (neat): 3531, 3056, 3019, 2962, 2902, 2865, 1467, 1432, 1391, 1270, 1220, 1184, 821, 769, 753 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 10% i PrOH, 90% hexane, 0.7 mL/min, 30 °C, 254 nm; 99% ee (t_R (major) = 7.93 min, t_R (minor) = 6.80 min).

SUPPORTING INFORMATION

Racemic



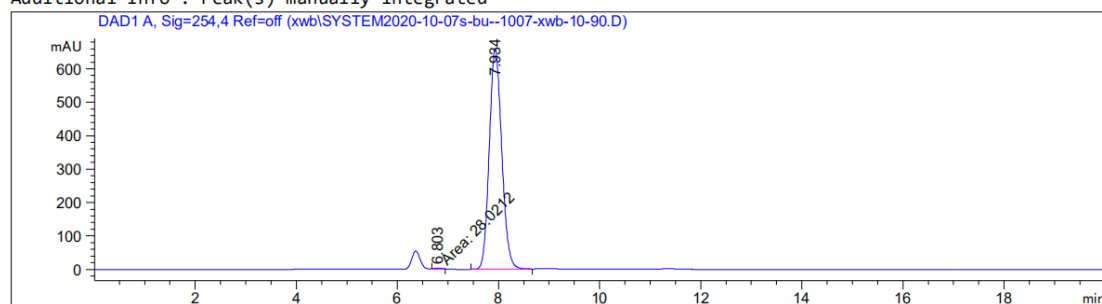
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.808	VB R	0.2440	7023.75586	448.74326	49.8920
2	7.963	BB	0.2767	7054.15723	394.36621	50.1080

Totals : 1.40779e4 843.10947

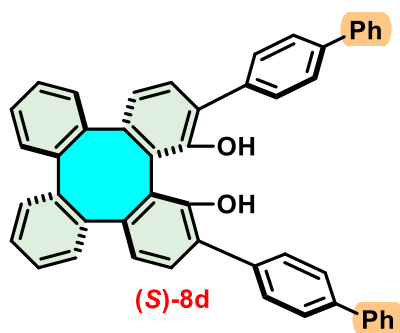
Enantioenriched

Additional Info : Peak(s) manually integrated



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.803	MM	0.1841	28.02122	2.53634	0.2477
2	7.934	BB	0.2660	1.12859e4	658.35449	99.7523



White solid. 538.0 mg, 84% yield. mp 161.0 – 161.5 °C. $[\alpha]_D^{25}$: +282.1 ($c = 1.0$, CHCl_3).

SUPPORTING INFORMATION

^1H NMR (600 MHz, CDCl_3) δ 7.66 – 7.58 (m, 6H), 7.43 (t, J = 7.8 Hz, 2H), 7.36 – 7.30 (m, 5H), 7.21 – 7.16 (m, 1H), 6.93 (d, J = 7.8 Hz, 1H), 5.33 (s, 1H).

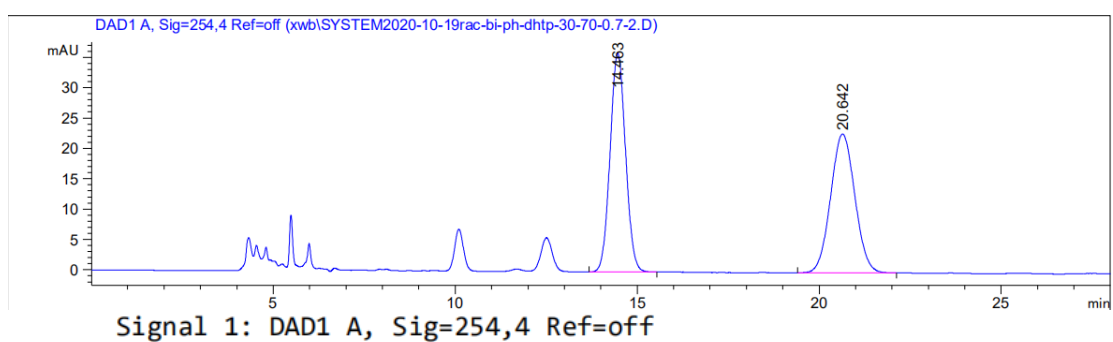
^{13}C NMR (150 MHz, CDCl_3) δ 149.28, 143.88, 141.45, 140.96, 140.73, 140.31, 136.27, 130.53, 129.70, 129.40, 128.83, 128.19, 127.65, 127.47, 127.40, 127.30, 127.12, 126.95, 122.34, 121.64.

HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{48}\text{H}_{31}\text{O}_2]^-$ 639.2330, found 639.2323.

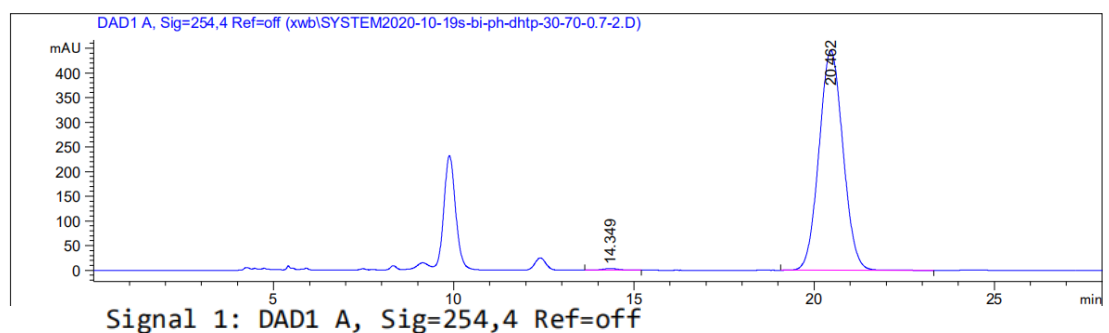
IR (neat): 3528, 3061, 3022, 2926, 2853, 1468, 1427, 1387, 1215, 1182, 1088, 906, 824, 752, 698, 667 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 30% *i*PrOH, 70% hexane, 0.7 mL/min, 30 °C, 254 nm; 99% *ee* (t_{R} (major) = 20.46 min, t_{R} (minor) = 14.35 min).

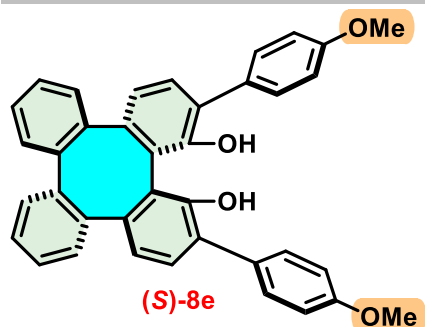
Racemic



Enantioenriched



SUPPORTING INFORMATION



White solid. 422.5 mg, 77% yield. mp 156.3 – 156.7 °C. $[\alpha]_D^{25}$: +203.5 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.44 (d, $J = 8.7$ Hz, 2H), 7.30 (d, $J = 3.2$ Hz, 3H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.18 – 7.14 (m, 1H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 7.8$ Hz, 1H), 5.25 (s, 1H), 3.81 (s, 3H).

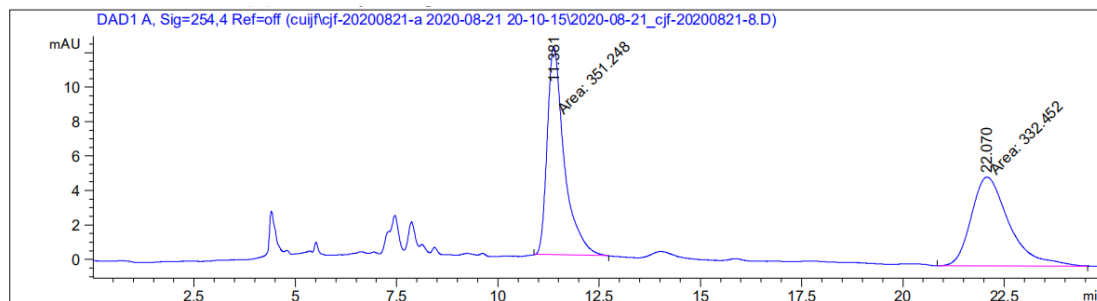
$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 159.04, 149.14, 143.29, 141.48, 141.09, 130.43, 130.29, 129.58, 129.32, 128.21, 127.51, 127.37, 126.96, 122.13, 121.69, 114.07, 55.33.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{38}\text{H}_{29}\text{O}_4]^+$ 549.2061, found 549.2061.

IR (neat): 3525, 3058, 2925, 2850, 1467, 1432, 1245, 1177, 1091, 905, 728, 650 cm^{-1} .

HPLC: Daicel Chiralpak[®] IC, 20% i PrOH, 80% hexane, 0.7 mL/min, 30 °C, 254 nm; 99% *ee* (t_R (major) = 11.33 min, t_R (minor) = 22.01 min).

Racemic



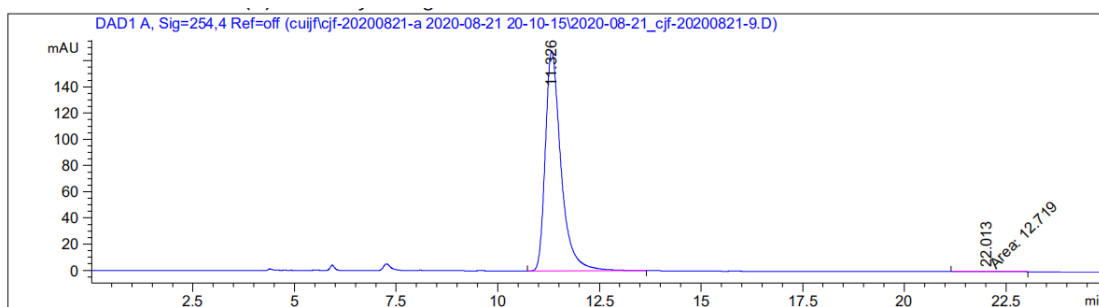
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.381	MM	0.4862	351.24780	12.04135	51.3746
2	22.070	MM	1.0784	332.45181	5.13782	48.6254

Totals : 683.69962 17.17917

SUPPORTING INFORMATION

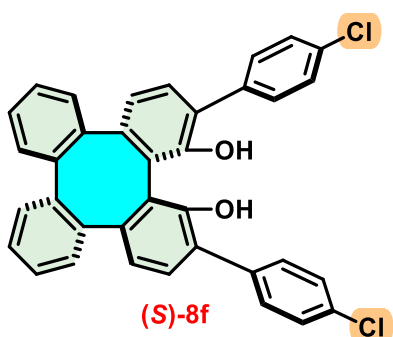
Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.326	BB	0.4055	4509.01758	167.79710	99.7187
2	22.013	MM	0.8218	12.71899	2.57959e-1	0.2813

Totals : 4521.73657 168.05506



White solid. 451.2 mg, 81% yield. mp 151.6 – 152.9 °C. $[\alpha]_{\text{D}}^{25}$: +197.6 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.27 (m, 3H), 7.24 (s, 1H), 7.19 – 7.12 (m, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 5.18 (s, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.11, 144.19, 141.33, 140.66, 135.71, 133.45, 130.68, 130.65, 129.46, 128.65, 128.09, 127.76, 127.52, 126.27, 122.46, 121.27.

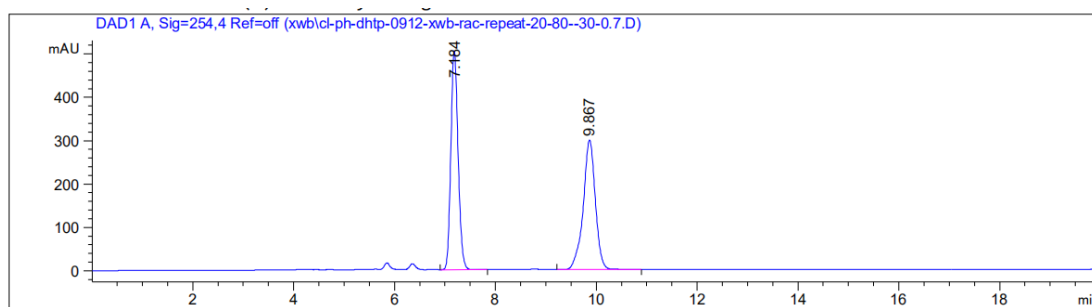
HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{36}\text{H}_{21}\text{Cl}_2\text{O}_2]^-$ 555.0924, found 555.0925.

IR (neat): 3528, 3058, 3016, 2925, 1468, 1432, 1387, 1215, 1183, 1093, 1014, 819, 751, 668 cm^{-1} .

HPLC: Daicel Chiralpak® AD-H, 20% i PrOH, 80% hexane, 0.7 mL/min, 30 °C, 254 nm; 98% *ee* (t_{R} (major) = 9.83 min, t_{R} (minor) = 7.18 min).

SUPPORTING INFORMATION

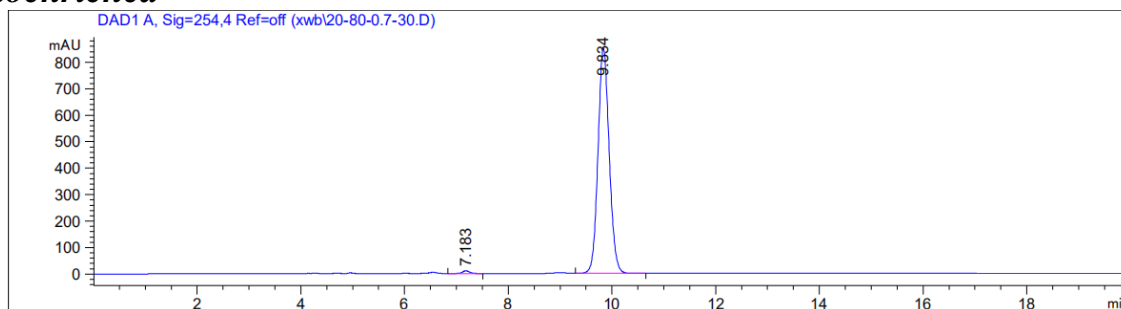
Racemic



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.184	BB	0.1545	5034.10840	504.10718	50.1169
2	9.867	BB	0.2515	5010.61572	299.04016	49.8831

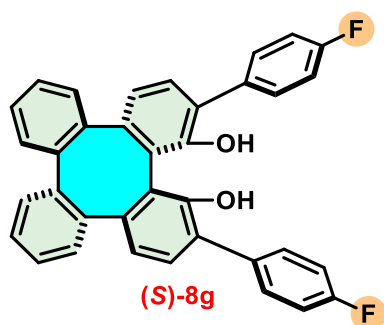
Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.183	BB	0.1506	98.24131	10.00159	0.7642
2	9.834	BB	0.2310	1.27566e4	850.65540	99.2358

Totals : 1.28548e4 860.65698



White solid. 393.1 mg, 75% yield. mp 128.0 – 128.5 °C. $[\alpha]_{\text{D}}^{25}$: +171.8 ($c = 1.0$, CHCl_3).

SUPPORTING INFORMATION

^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.46 (m, 2H), 7.35 – 7.28 (m, 3H), 7.25 (d, $J = 4.4$ Hz, 1H), 7.19 – 7.14 (m, 1H), 7.13 – 7.04 (m, 2H), 6.91 (d, $J = 7.8$ Hz, 1H), 5.18 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.25 (d, $J = 246.8$ Hz), 149.09, 143.92, 141.37, 140.75, 133.20 (d, $J = 3.3$ Hz), 130.99 (d, $J = 8.0$ Hz), 130.67, 129.42, 128.10, 127.69, 127.47, 126.43, 122.35, 121.34, 115.41 (d, $J = 21.3$ Hz).

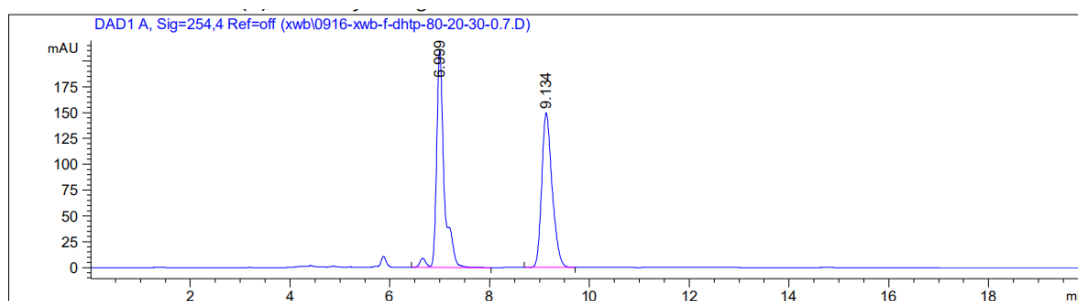
^{19}F NMR (376 MHz, CDCl_3) δ -114.79.

HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{36}\text{H}_{21}\text{F}_2\text{O}_2]^-$ 523.1515, found 523.1512.

IR (neat): 3530, 3061, 3017, 2928, 2857, 1517, 1468, 1432, 1384, 1227, 1184, 1160, 908, 822, 750 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 20% i PrOH, 80% hexane, 0.7 mL/min, 30 $^\circ\text{C}$, 254 nm; 98% *ee* (t_{R} (major) = 9.07 min, t_{R} (minor) = 6.95 min).

Racemic

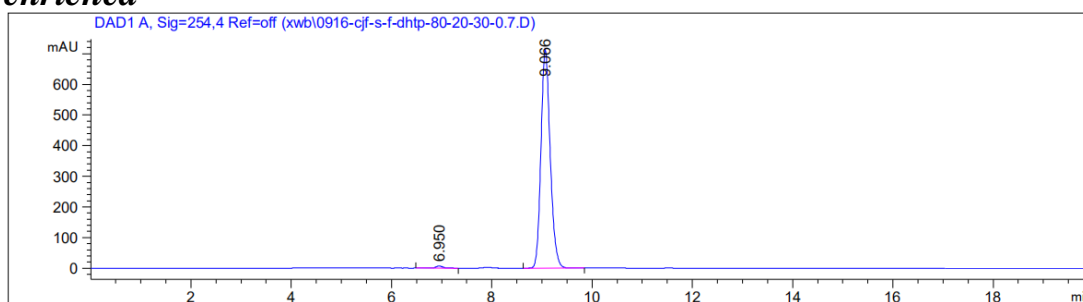


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.999	VV R	0.1517	2254.13013	209.36095	50.9606
2	9.134	BB	0.2191	2169.14990	149.65433	49.0394

Totals : 4423.28003 359.01527

Enantioenriched

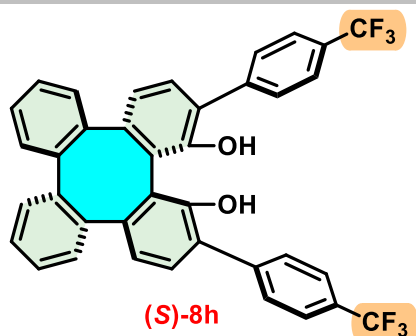


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.950	VB R	0.1442	79.14410	7.35916	0.8597
2	9.066	BB	0.1974	9127.18848	712.86774	99.1403

Totals : 9206.33257 720.22690

SUPPORTING INFORMATION



White solid. 437.5 mg, 70% yield. mp 128.3 – 128.5 °C. $[\alpha]_D^{25}$: +162.6 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.65 (s, 4H), 7.36 – 7.29 (m, 4H), 7.20 – 7.16 (m, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 5.18 (s, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.20, 144.76, 141.25, 140.96, 140.43, 130.98, 129.65, 129.53, 129.45 (q, $J = 32.5$ Hz), 128.01, 127.89, 127.58, 126.15, 125.29 (q, $J = 3.7$ Hz), 124.21 (q, $J = 271.9$ Hz), 122.65, 121.03.

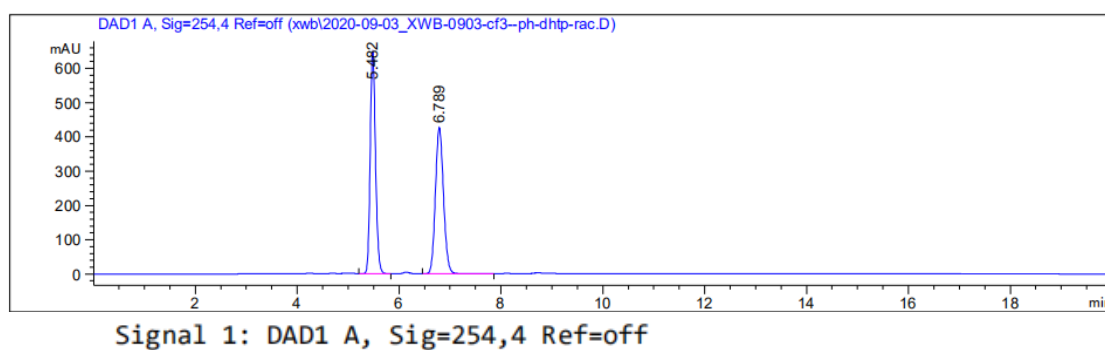
$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -62.50.

HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{38}\text{H}_{21}\text{F}_6\text{O}_2]^-$ 623.1451, found 623.1451.

IR (neat): 538, 3061, 3017, 2930, 2852, 1617, 1386, 1325, 1215, 1167, 1125, 852, 824, 751, 668 cm^{-1} .

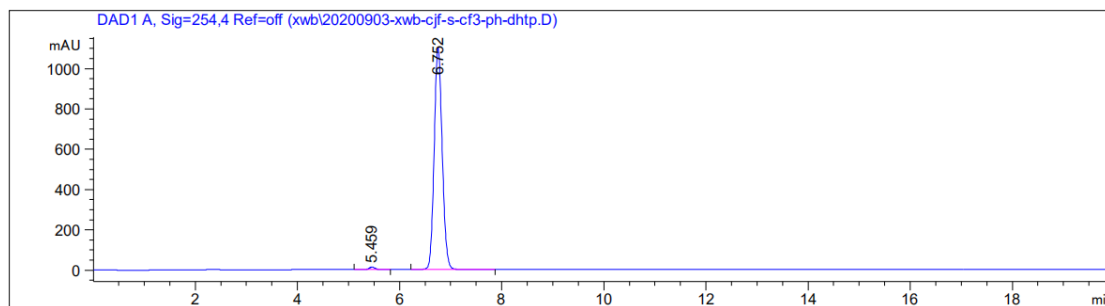
HPLC: Daicel Chiralpak[®] AD-H, 20% *i*PrOH, 80% hexane, 0.7 mL/min, 30 °C, 254 nm; 98% *ee* (t_R (major) = 6.75 min, t_R (minor) = 5.46 min).

Racemic



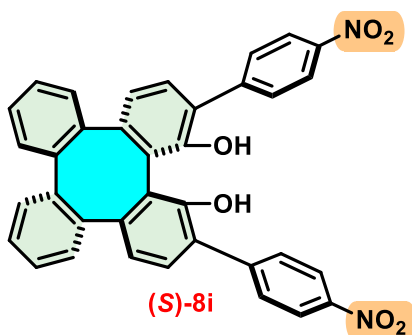
SUPPORTING INFORMATION

Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.459	BB	0.1199	99.67613	12.65129	0.8217
2	6.752	BB	0.1695	1.20312e4	1100.59680	99.1783



Pale yellow solid. 497.3 mg, 86% yield. mp 281.2 – 281.7 °C. $[\alpha]_D^{25}$: +241.3 ($c = 1.0$, CHCl_3)

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.20 (d, $J = 8.8$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.37 – 7.29 (m, 4H), 7.18 (dq, $J = 7.1, 3.7$ Hz, 1H), 6.99 (d, $J = 7.9$ Hz, 1H), 5.34 (s, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.40, 146.83, 145.56, 144.18, 141.13, 140.13, 131.21, 130.18, 129.65, 128.10, 127.94, 127.71, 125.44, 123.48, 122.90, 120.84.

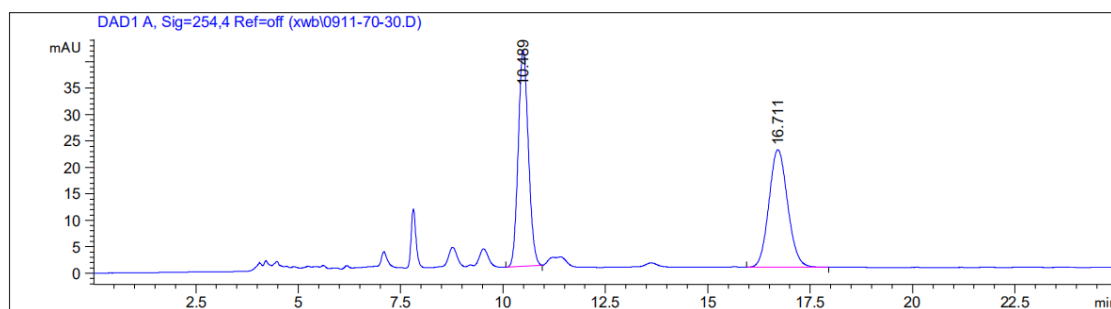
HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{36}\text{H}_{21}\text{N}_2\text{O}_6]^-$ 577.1405, found 577.1399.

IR (neat): 3515, 3061, 2928, 1597, 1515, 1435, 1387, 1345, 1220, 1182, 858, 772, 754 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 30% i PrOH, 70% hexane, 0.7 mL/min, 30 °C, 254 nm; 98% ee (t_R (major) = 16.66 min, t_R (minor) = 10.47 min).

SUPPORTING INFORMATION

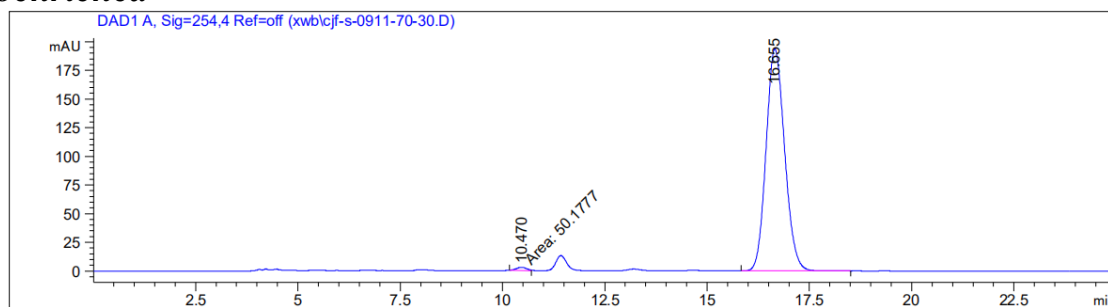
Racemic



Signal 1: DAD1 A, Sig=254,4 Ref=off

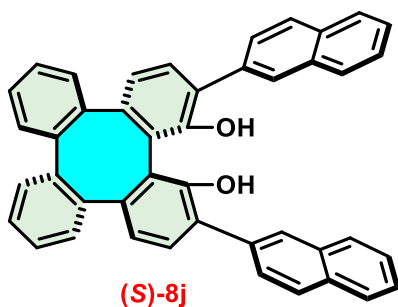
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.489	BB	0.2672	704.39783	40.84756	49.9107
2	16.711	BB	0.4925	706.91888	22.25986	50.0893

Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.470	MM	0.2931	50.17770	2.85312	0.8140
2	16.655	BB	0.4906	6114.48926	193.53551	99.1860



White solid. 447.2 mg, 76% yield. mp 169.2 – 171.1 °C. $[\alpha]_D^{25}$: +228.0 ($c = 0.5$, CHCl_3).

SUPPORTING INFORMATION

^1H NMR (600 MHz, CDCl_3) δ 7.98 (s, 1H), 7.87 (d, $J = 8.5$ Hz, 1H), 7.82 (ddd, $J = 9.5, 6.1, 3.4$ Hz, 2H), 7.65 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.47 (dq, $J = 6.8, 3.5$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 1H), 7.37 – 7.32 (m, 3H), 7.22 – 7.18 (m, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 5.42 (s, 1H).

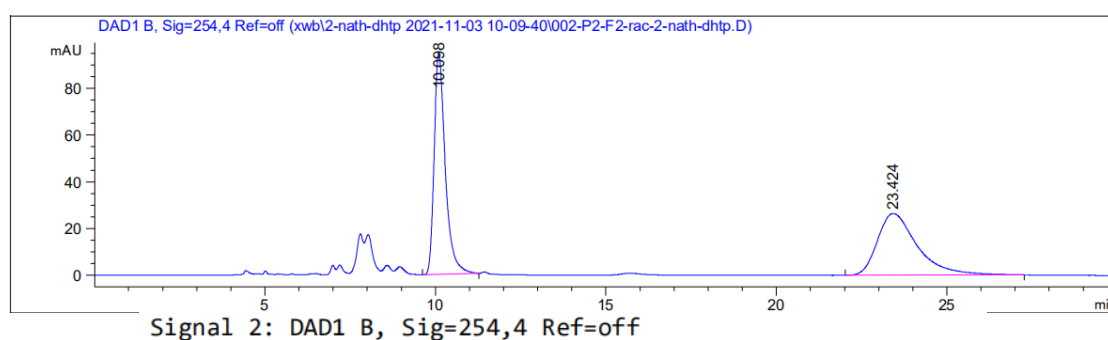
^{13}C NMR (150 MHz, CDCl_3) δ 149.40, 143.90, 141.47, 141.02, 134.82, 133.49, 132.61, 130.78, 129.39, 128.25, 128.17, 128.11, 127.66, 127.65, 127.47, 127.30, 126.28, 126.16, 122.36, 121.83.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{44}\text{H}_{29}\text{O}_2]^+$ 589.2162, found 589.2164.

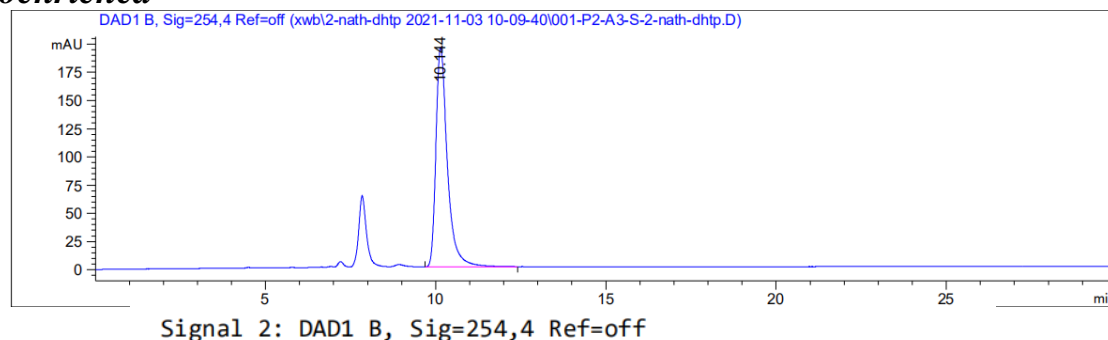
IR (neat): 3530, 3058, 3019, 2928, 2852, 1436, 1228, 906, 818, 731, 650 cm^{-1} .

HPLC: Daicel Chiralpak[®] IC, 10% i PrOH, 90% hexane, 0.7 mL/min, 30 $^\circ\text{C}$, 254 nm; >99% *ee* (t_{R} (major) = 10.14 min).

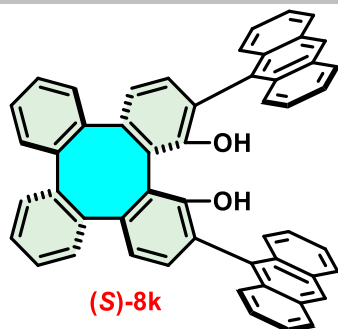
Racemic



Enantioenriched



SUPPORTING INFORMATION



White solid. 496.0 mg, 72% yield. mp 233.8 – 234.0 °C. $[\alpha]_D^{25}$: +85.8 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.48 (s, 1H), 8.00 (dd, $J = 13.5, 8.5$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.52 (d, $J = 7.3$ Hz, 1H), 7.49 – 7.41 (m, 3H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.21 – 7.16 (m, 2H), 7.04 (d, $J = 7.6$ Hz, 1H), 4.78 (s, 1H).

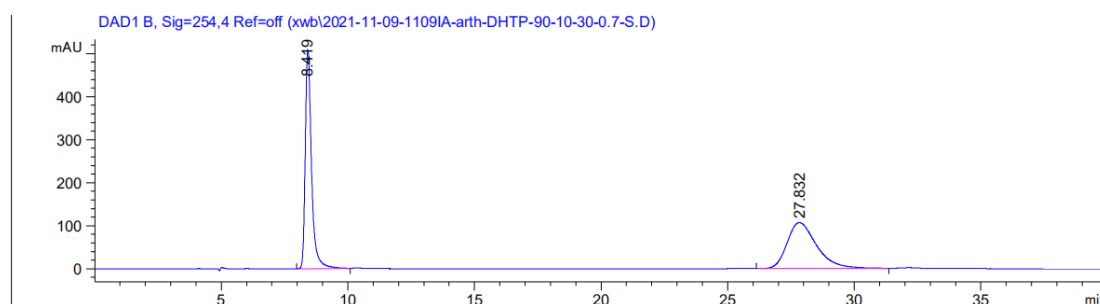
$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 150.48, 144.27, 141.75, 141.53, 131.64, 131.55, 131.45, 130.72, 130.59, 130.55, 128.93, 128.52, 128.50, 127.91, 127.58, 127.57, 127.19, 126.19, 126.13, 126.07, 126.01, 125.35, 125.32, 123.38, 123.03, 121.59.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{52}\text{H}_{33}\text{O}_2]^+$ 689.2476, found 689.2479.

IR (neat): 3513, 3053, 2923, 1558, 1436, 1409, 1310, 1238, 1219, 903, 772, 739 cm^{-1} .

HPLC: Daicel Chiralpak[®] IA, 10% i PrOH, 90% hexane, 0.7 mL/min, 30 °C, 254 nm; >99% *ee* (t_R (major) = 8.41 min).

Racemic



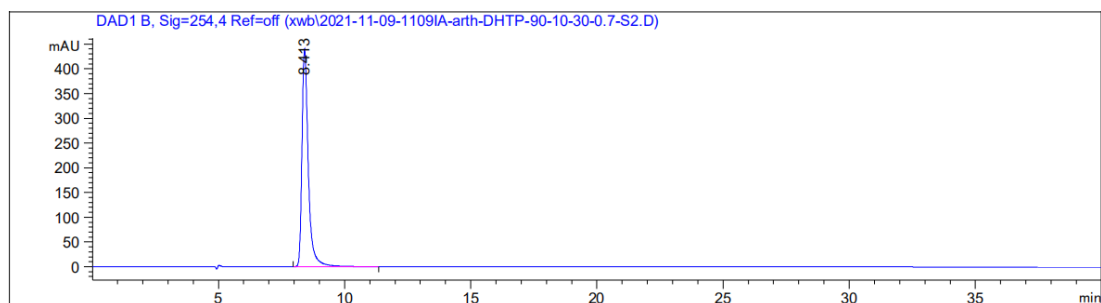
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.419	BB	0.2600	8708.83496	507.92249	50.2215
2	27.832	BB	1.2154	8632.01660	106.74400	49.7785

Totals : 1.73409e4 614.66649

SUPPORTING INFORMATION

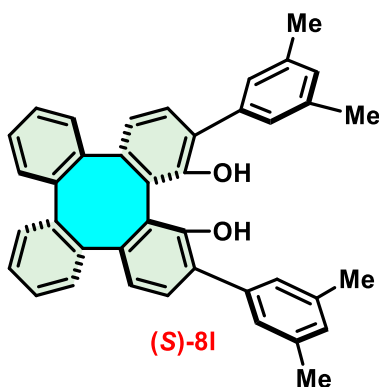
Enantioenriched



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.413	BB	0.2625	7717.76953	440.25717	100.0000

Totals : 7717.76953 440.25717



White solid. 490.2 mg, 90% yield. mp 154.0 – 155.3 °C. $[\alpha]_D^{25}$: +167.4 ($c = 0.5$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34 – 7.28 (m, 3H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.19 – 7.14 (m, 1H), 7.11 (s, 2H), 6.97 (s, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 5.32 (s, 1H), 2.32 (s, 6H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.14, 143.48, 141.50, 141.20, 138.31, 137.16, 130.13, 129.30, 129.23, 128.27, 127.48, 127.42, 127.34, 127.01, 122.01, 21.36.

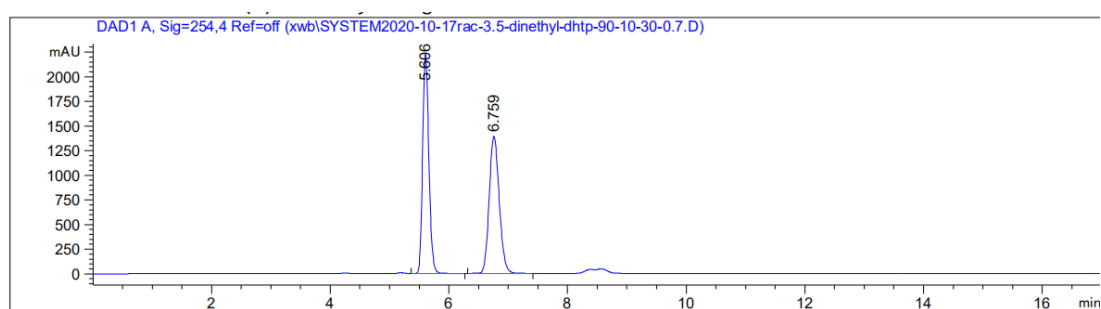
HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{40}\text{H}_{33}\text{O}_2]^+$ 545.2476, found 545.2479.

IR (neat): 3529, 3061, 3017, 2917, 2855, 1601, 1468, 1435, 1393, 1297, 1237, 1215, 1181, 855, 822, 750, 707 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 10% i PrOH, 90% hexane, 0.7 mL/min, 30 °C, 254 nm; 98% *ee* (t_R (major) = 5.57 min, t_R (minor) = 6.71 min).

SUPPORTING INFORMATION

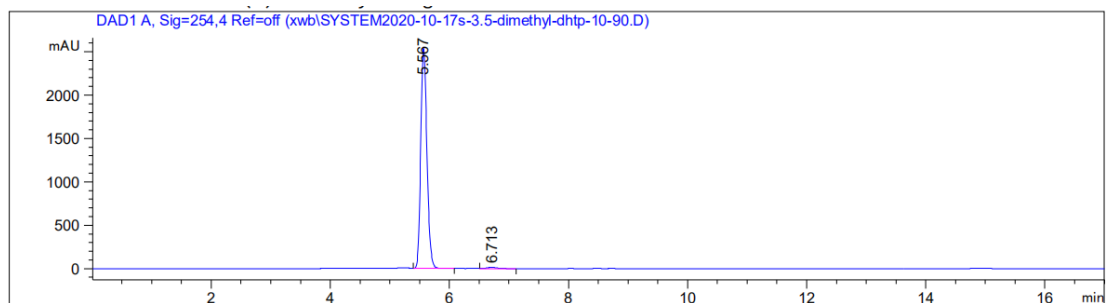
Racemic



Signal 1: DAD1 A, Sig=254,4 Ref=off

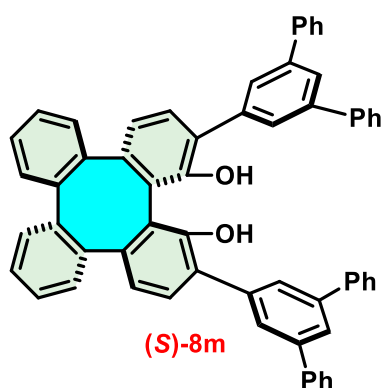
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.606	VB	0.1131	1.62048e4	2222.23950	49.7188
2	6.759	VB R	0.1833	1.63881e4	1390.87524	50.2812

Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.567	BB	0.1102	1.82920e4	2533.75903	99.1458
2	6.713	VB	0.1771	157.59810	13.81514	0.8542



White solid. 618.6 mg, 78% yield. mp 280.2 – 282.0 °C. $[\alpha]_D^{25}$: +145.1 ($c = 1.0$, CHCl_3).

SUPPORTING INFORMATION

^1H NMR (600 MHz, CDCl_3) δ 7.76 – 7.74 (m, 3H), 7.65 (d, $J = 7.7$ Hz, 4H), 7.46 – 7.39 (m, 5H), 7.38 – 7.32 (m, 5H), 7.21 – 7.18 (m, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 5.40 (s, 1H).

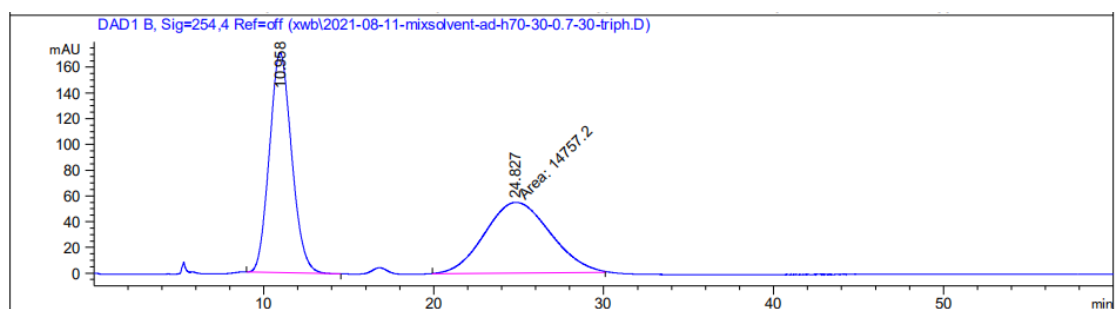
^{13}C NMR (150 MHz, CDCl_3) δ 149.35, 144.09, 142.19, 141.44, 140.96, 138.26, 130.67, 129.42, 128.82, 128.25, 127.68, 127.54, 127.48, 127.39, 127.20, 125.33, 122.39, 121.74.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{60}\text{H}_{41}\text{O}_2]^+$ 793.3102, found 793.3104.

IR (neat): 528, 3061, 3017, 2925, 1594, 1497, 1400, 1216, 1182, 1076, 884, 753, 699, 669 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 30% i PrOH, 70% hexane, 0.7 mL/min, 30 °C, 254 nm; >99% ee (t_R (major) = 11.16 min).

Racemic

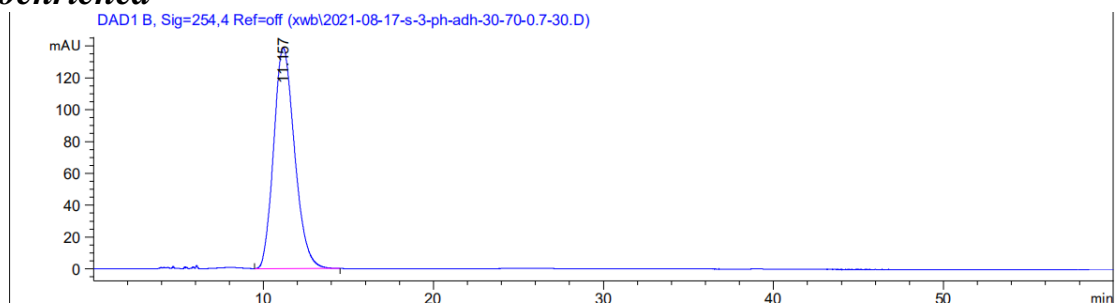


Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.958	BB	1.3634	1.55458e4	170.88400	51.3012
2	24.827	MM	4.4781	1.47572e4	54.92372	48.6988

Totals : 3.03030e4 225.80772

Enantioenriched



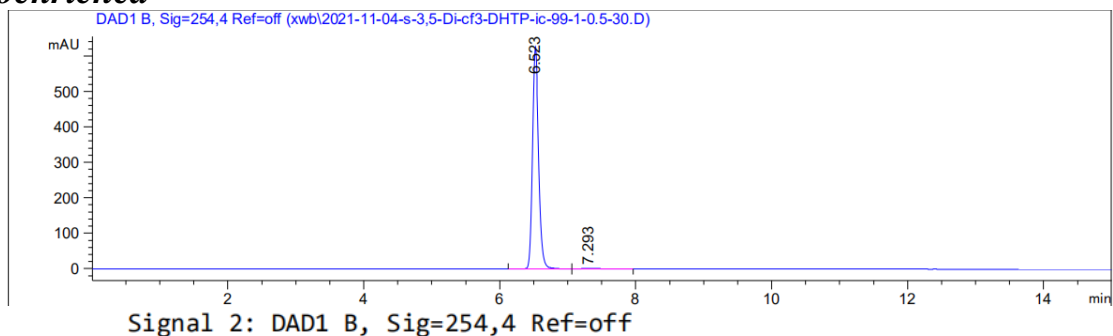
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.157	BB	1.3071	1.18721e4	138.63240	100.0000

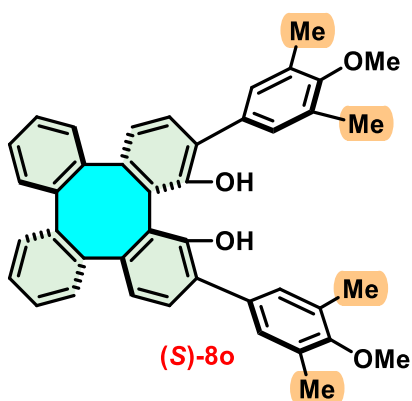
Totals : 1.18721e4 138.63240

SUPPORTING INFORMATION

Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.523	BB	0.0980	3968.85254	625.66522	99.3665
2	7.293	BB	0.2526	25.30327	1.37586	0.6335
Totals :				3994.15581	627.04108	



White solid. 513.9 mg, 85% yield. mp 152.6 – 153.7 °C. $[\alpha]_D^{25}$: +164.8 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.30 (t, $J = 4.2$ Hz, 3H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 3H), 6.86 (d, $J = 7.8$ Hz, 1H), 5.30 (s, 1H), 3.73 (s, 3H), 2.29 (s, 6H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 156.48, 149.09, 143.38, 141.48, 141.13, 132.67, 131.17, 130.17, 129.70, 129.30, 128.23, 127.49, 127.34, 127.02, 122.03, 121.82, 59.72, 16.16.

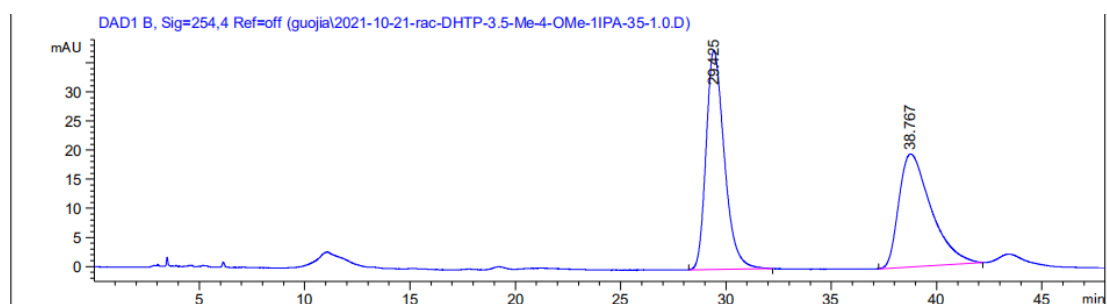
HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{42}\text{H}_{37}\text{O}_4]^+$ 605.2687, found 605.2689.

IR (neat): 3528, 3056, 3014, 2930, 2855, 2826, 1481, 1467, 1435, 1242, 1203, 1166, 750 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 1% *i*PrOH, 99% hexane, 1.0 mL/min, 40 °C, 254 nm; 99% *ee* (t_R (major) = 29.08 min, t_R (minor) = 39.18 min).

SUPPORTING INFORMATION

Racemic

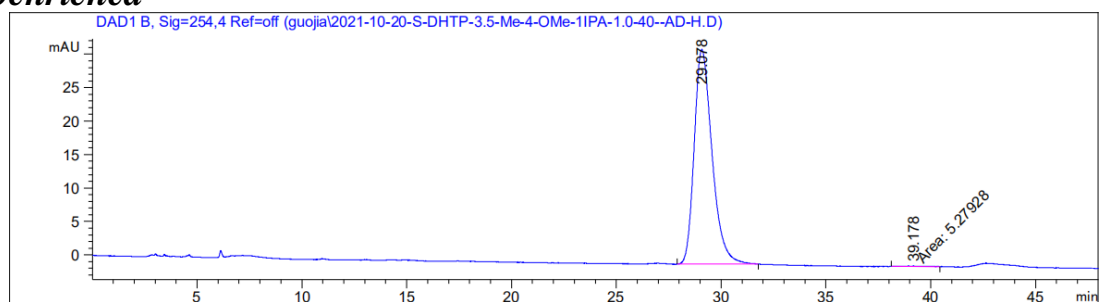


Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.425	BB	0.9190	2267.25439	37.62780	52.4103
2	38.767	BB	1.2617	2058.71655	19.40524	47.5897

Totals : 4325.97095 57.03304

Enantioenriched

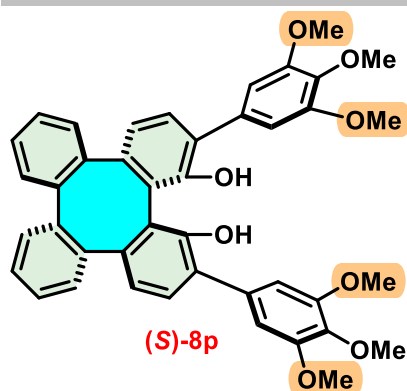


Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.078	BB	0.8834	1900.56519	32.06894	99.7230
2	39.178	MM	1.1793	5.27928	7.46120e-2	0.2770

Totals : 1905.84447 32.14355

SUPPORTING INFORMATION



White solid. 501.6 mg, 75% yield. mp 153.5 – 154.6 °C. $[\alpha]_D^{25}$: +131.2 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 7.43 – 7.36 (m, 3H), 7.33 (d, $J = 7.8$ Hz, 1H), 7.26 – 7.20 (m, 1H), 6.93 (d, $J = 7.8$ Hz, 1H), 6.75 (s, 2H), 5.53 (s, 1H), 3.86 (s, 6H), 3.83 (s, 3H).

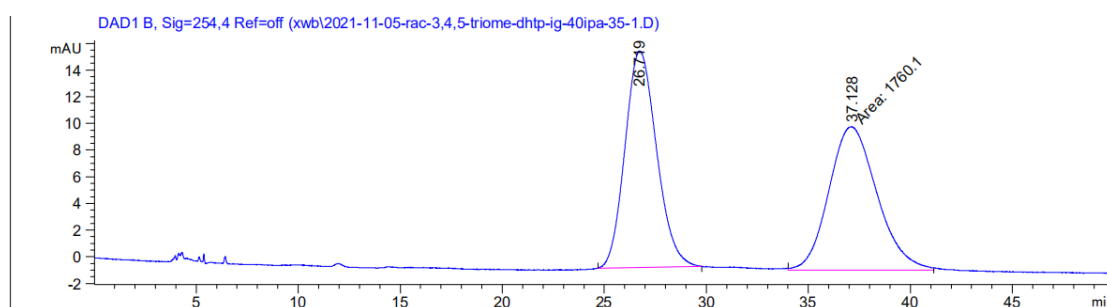
$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 153.43, 149.10, 143.72, 141.43, 141.01, 137.55, 132.73, 130.12, 129.41, 128.34, 127.60, 127.38, 127.17, 122.17, 122.08, 106.46, 60.91, 56.24.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{42}\text{H}_{37}\text{O}_8]^+$ 669.2483, found 669.2487.

IR (neat): 3528, 3058, 3014, 2936, 2834, 1585, 1511, 1466, 1430, 1402, 1347, 1238, 1126, 1004, 750 cm^{-1} .

HPLC: Daicel Chiralpak[®] IG, 60% i PrOH, 40% hexane, 0.7 mL/min, 35 °C, 254 nm; >99% ee (t_R (major) = 26.43 min).

Racemic



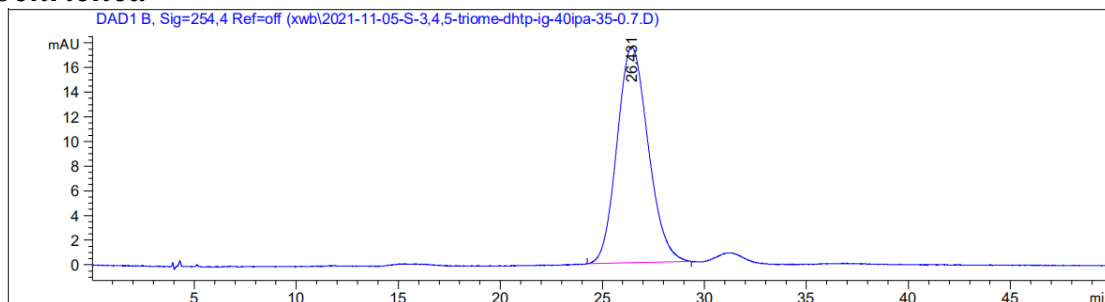
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.719	BB	1.2793	1747.35352	16.21451	49.8183
2	37.128	MM	2.7274	1760.09717	10.75579	50.1817

Totals : 3507.45068 26.97030

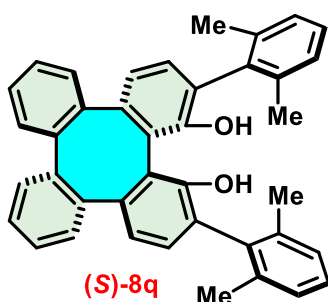
SUPPORTING INFORMATION

Enantioenriched



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.431	BB	1.2686	1860.26758	17.49457	100.0000
Totals :				1860.26758	17.49457	



White solid. 305.0 mg, 56% yield. mp 141.2 – 143.0 °C. $[\alpha]_D^{25}$: +103.3 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (ddd, $J = 19.9, 5.6, 3.4$ Hz, 3H), 7.19 – 7.02 (m, 4H), 6.94 (d, $J = 7.7$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 4.70 (s, 1H), 2.09 (s, 3H), 1.74 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.96, 143.42, 141.62, 141.40, 137.60, 137.39, 135.72, 129.47, 128.78, 128.01, 127.67, 127.65, 127.63, 127.25, 127.05, 125.71, 122.30, 121.49, 20.64, 19.85.

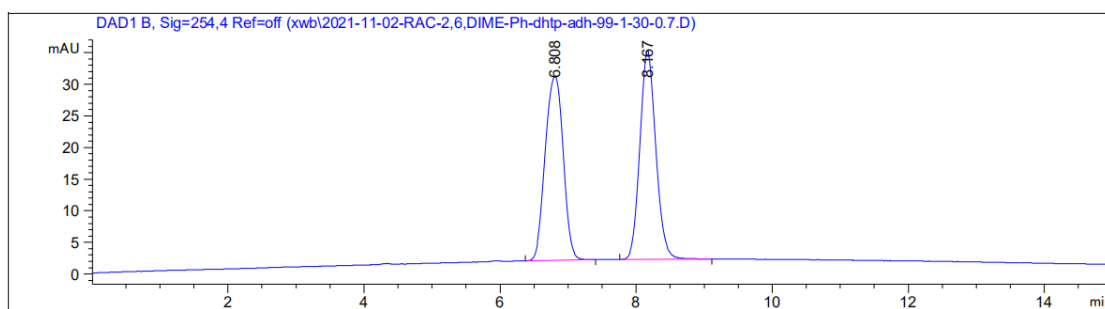
HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{40}\text{H}_{33}\text{O}_2]^+$ 545.2476, found 545.2477.

IR (neat): 3533, 3058, 3014, 2917, 2857, 1464, 1437, 1296, 1216, 1183, 1084, 906, 824, 750, 668 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 1% i PrOH, 99% hexane, 0.7 mL/min, 30 °C, 254 nm; >99% *ee* (t_R (major) = 6.99 min).

SUPPORTING INFORMATION

Racemic

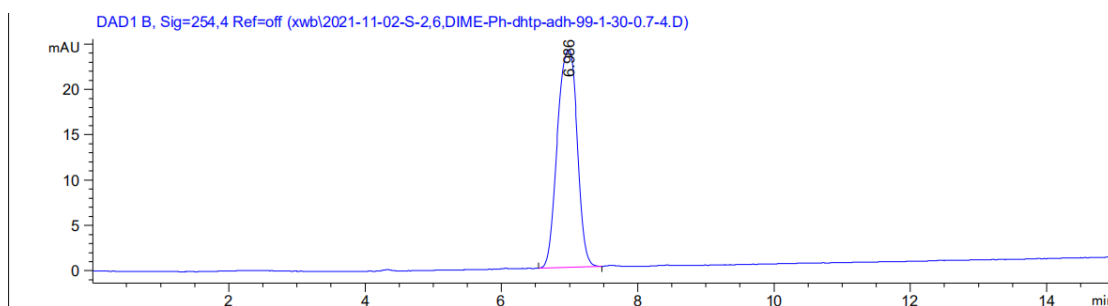


Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.808	BB	0.2971	536.65985	29.11122	49.9223
2	8.167	BB	0.2525	538.32965	32.96986	50.0777

Totals : 1074.98950 62.08108

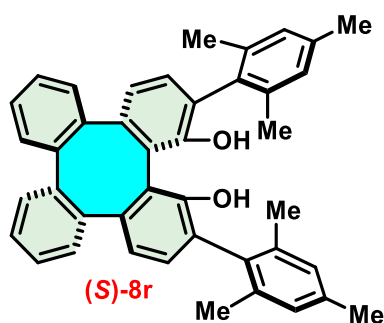
Enantioenriched



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.986	BB	0.3298	484.56012	23.97944	100.0000

Totals : 484.56012 23.97944



White solid. 240.5 mg, 42% yield. mp 142.1 – 143.0 °C. $[\alpha]_D^{25}$: +87.2 ($c = 0.5$, CHCl_3).

SUPPORTING INFORMATION

^1H NMR (600 MHz, CDCl_3) δ 7.34 – 7.30 (m, 1H), 7.30 – 7.26 (m, 2H), 7.18 – 7.14 (m, 1H), 6.95 – 6.91 (m, 2H), 6.89 (s, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 4.72 (s, 1H), 2.29 (s, 3H), 2.05 (s, 3H), 1.71 (s, 3H).

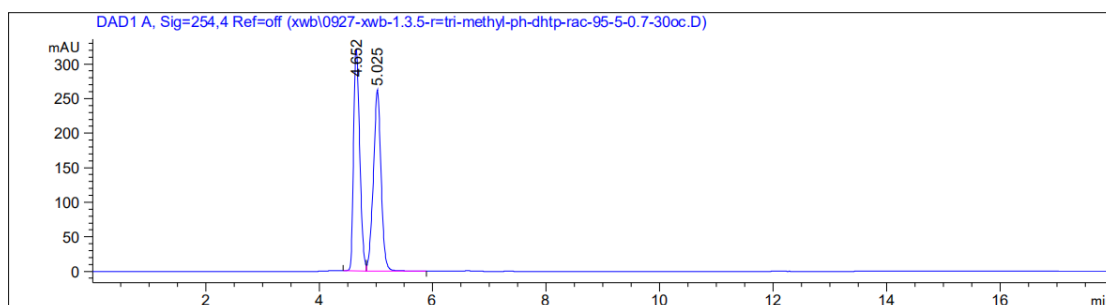
^{13}C NMR (150 MHz, CDCl_3) δ 149.08, 143.25, 141.59, 141.41, 137.55, 137.43, 137.20, 132.68, 129.66, 128.74, 128.43, 127.68, 127.17, 126.99, 125.66, 122.18, 121.39, 21.11, 20.48, 19.73.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{42}\text{H}_{37}\text{O}_2]^+$ 573.2789, found 573.2790.

IR (neat): 3529, 3056, 3014, 2921, 2857, 1558, 1458, 1437, 1219, 1084, 904, 852, 770, 753 cm^{-1} .

HPLC: Daicel Chiralpak[®] AD-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 30 °C, 254 nm; 99% *ee* (t_{R} (major) = 5.08 min, t_{R} (minor) = 4.61 min).

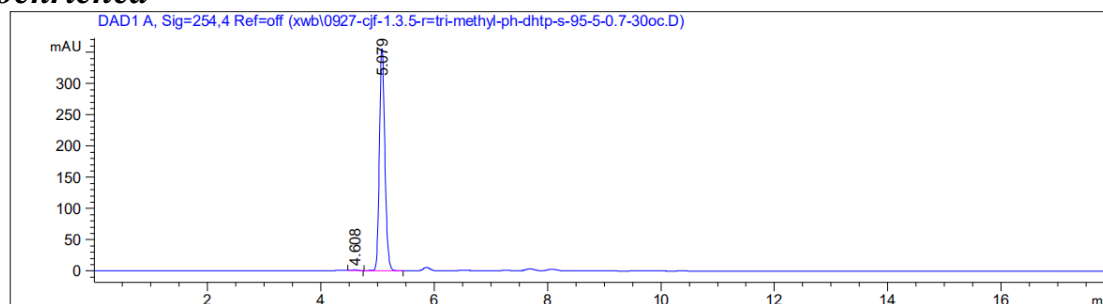
Racemic



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.652	BV	0.1207	2430.43530	319.75024	49.4706
2	5.025	VB	0.1405	2482.45776	262.20929	50.5294

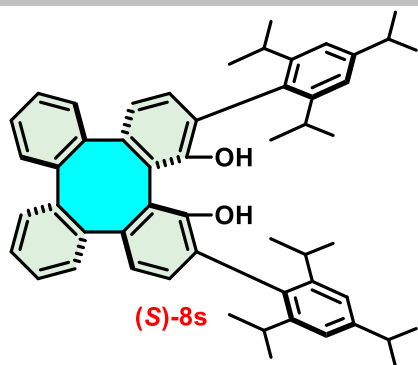
Enantioenriched



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.608	BB	0.0799	9.01947	1.55030	0.3772
2	5.079	BB	0.1021	2381.87036	355.84863	99.6228

SUPPORTING INFORMATION



This compound was prepared following modified procedure.

White solid. 555.6 mg, 75% yield. mp 143.5 – 144.6 °C. $[\alpha]_D^{25}$: +99.6 ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 (dd, $J = 5.7, 3.2$ Hz, 1H), 7.35 – 7.27 (m, 2H), 7.23 – 7.15 (m, 1H), 7.10 (s, 1H), 7.05 (s, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.6$ Hz, 1H), 4.64 (s, 1H), 3.03 – 2.76 (m, 2H), 2.22 – 2.04 (m, 1H), 1.31 (d, $J = 6.9$ Hz, 6H), 1.14 (d, $J = 6.8$ Hz, 3H), 1.10 (d, $J = 7.0$ Hz, 3H), 0.90 (d, $J = 6.9$ Hz, 3H), 0.85 (d, $J = 6.8$ Hz, 3H).

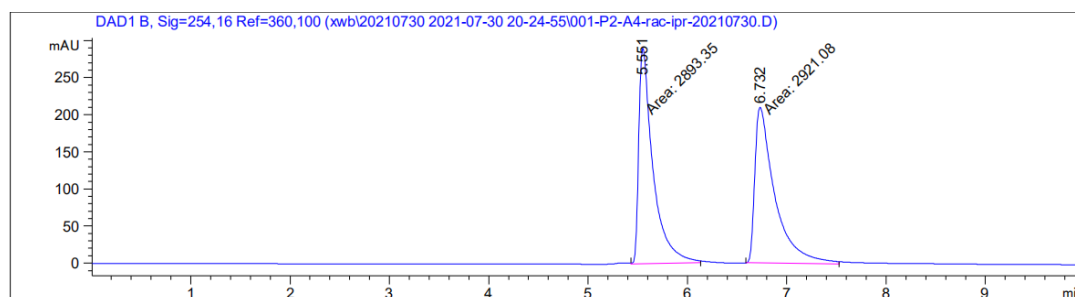
$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.90, 148.82, 147.96, 147.73, 143.04, 141.73, 141.56, 130.49, 130.01, 128.49, 127.11, 126.94, 126.82, 124.99, 122.23, 121.20, 121.07, 120.43, 34.31, 30.71, 30.18, 24.37, 24.06, 24.01, 23.95, 23.68, 23.68.

HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{54}\text{H}_{59}\text{O}_2]^-$ 739.4520, found 739.4514.

IR (neat): 3529, 3058, 3021, 2961, 2925, 2868, 1558, 1458, 1429, 1216, 770, 668 cm^{-1} .

HPLC: Daicel Chiralpak[®] IA, 0.1% i PrOH, 99.9 % hexane, 0.7 mL/min, 30 °C, 254 nm; 98% ee (t_R (major) = 6.58 min).

Racemic



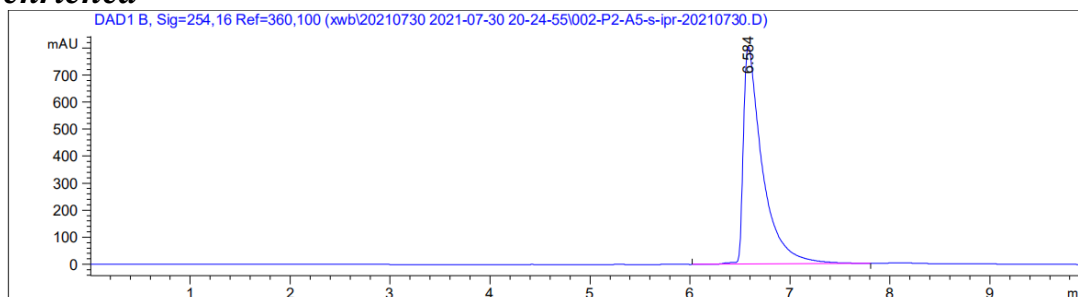
Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.551	MM	0.1662	2893.35449	290.08139	49.7616
2	6.732	MM	0.2320	2921.08276	209.86952	50.2384

Totals : 5814.43726 499.95091

SUPPORTING INFORMATION

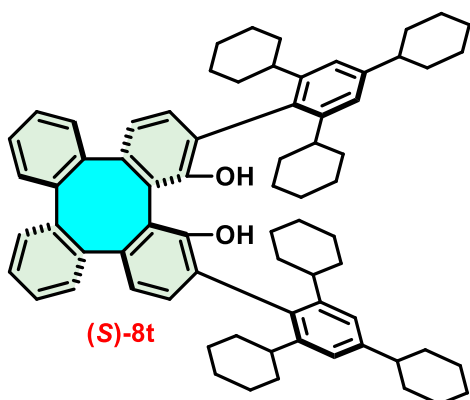
Enantioenriched



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.584	VB R	0.1881	1.06157e4	803.48834	100.0000

Totals : 1.06157e4 803.48834



This compound was prepared following modified procedure.

White solid. 687.0 mg, 70% yield. mp 154.4 – 154.8 °C. $[\alpha]_D^{25}$: +107.4 ($c = 0.5$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.32 (d, $J = 6.8$ Hz, 1H), 7.23 – 7.16 (m, 2H), 7.07 (d, $J = 7.0$ Hz, 1H), 6.94 (s, 1H), 6.89 (s, 1H), 6.82 (d, $J = 7.7$ Hz, 1H), 6.74 (d, $J = 7.6$ Hz, 1H), 4.47 (s, 1H), 2.42 (ddd, $J = 11.5, 8.1, 3.4$ Hz, 1H), 2.31 (td, $J = 10.3, 8.7, 6.0$ Hz, 1H), 1.85 (d, $J = 11.8$ Hz, 2H), 1.77 (d, $J = 12.4$ Hz, 2H), 1.72 – 1.61 (m, 3H), 1.52 – 1.12 (m, 17H), 1.12 – 0.92 (m, 5H), 0.66 (q, $J = 12.9$ Hz, 1H), 0.43 (q, $J = 12.7$ Hz, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.99, 147.65, 146.99, 146.92, 142.97, 141.79, 141.77, 130.91, 130.18, 128.85, 127.41, 127.29, 126.76, 124.85, 122.21, 122.19, 122.04, 120.44, 44.74, 41.48, 41.17, 34.58, 34.55, 34.50, 34.48, 34.43, 33.81, 27.04, 27.01, 26.84, 26.79, 26.59, 26.27, 26.17, 26.10.

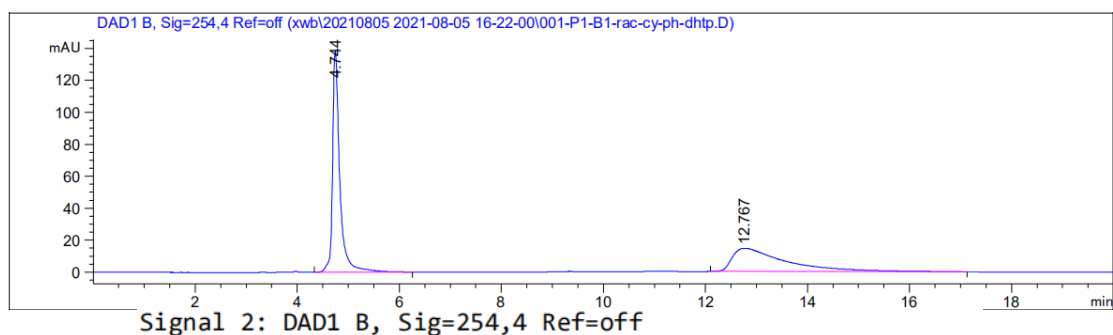
HRMS (ESI): $[\text{M}-\text{H}]^-$ Calcd. for $[\text{C}_{72}\text{H}_{83}\text{O}_2]^-$ 979.6398, found 979.6390.

IR (neat): 3529, 3056, 2960, 2928, 2869, 1558, 1460, 1429, 1362, 1306, 1218, 1084, 906, 878, 751, 668 cm^{-1} .

SUPPORTING INFORMATION

HPLC: Daicel Chiralpak® IA, 0.2% *i*PrOH, 99.8 % hexane, 1.0 mL/min, 30 °C, 254 nm; 99% *ee* (t_R (major) = 12.33 min, t_R (minor) = 4.80 min).

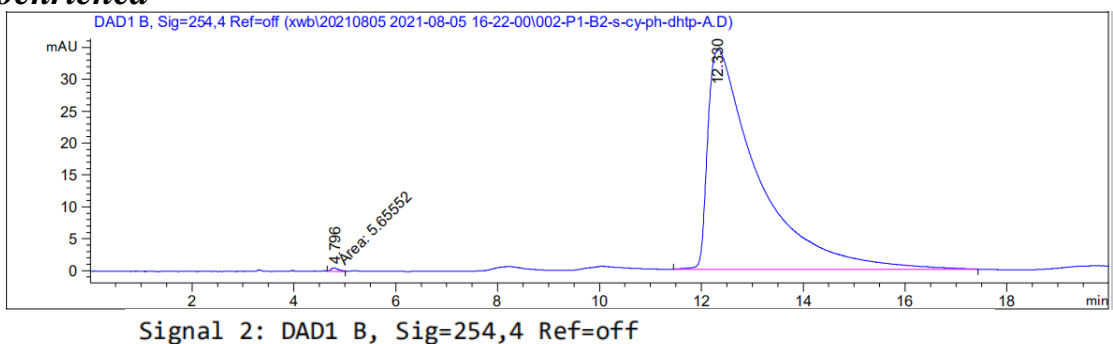
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.744	BB	0.1425	1362.87305	138.91057	56.2200
2	12.767	BB	0.9832	1061.30347	14.54588	43.7800

Totals : 2424.17651 153.45645

Enantioenriched



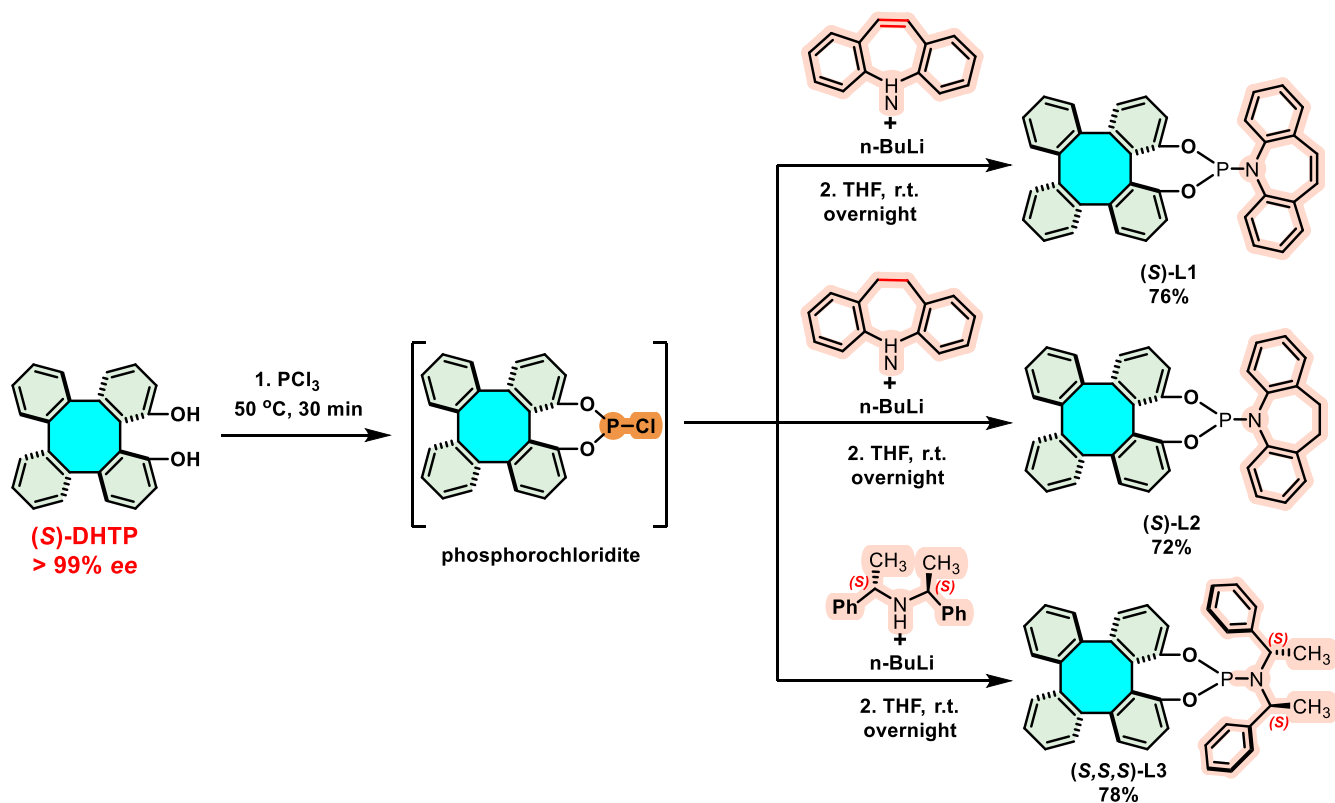
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.796	MM	0.1792	5.65552	5.26025e-1	0.2387
2	12.330	BB	0.9304	2363.34717	34.44713	99.7613

Totals : 2369.00269 34.97315

SUPPORTING INFORMATION

General Procedure for Synthesis of (*S*)-DHTP Derived Phosphoramidite Ligands

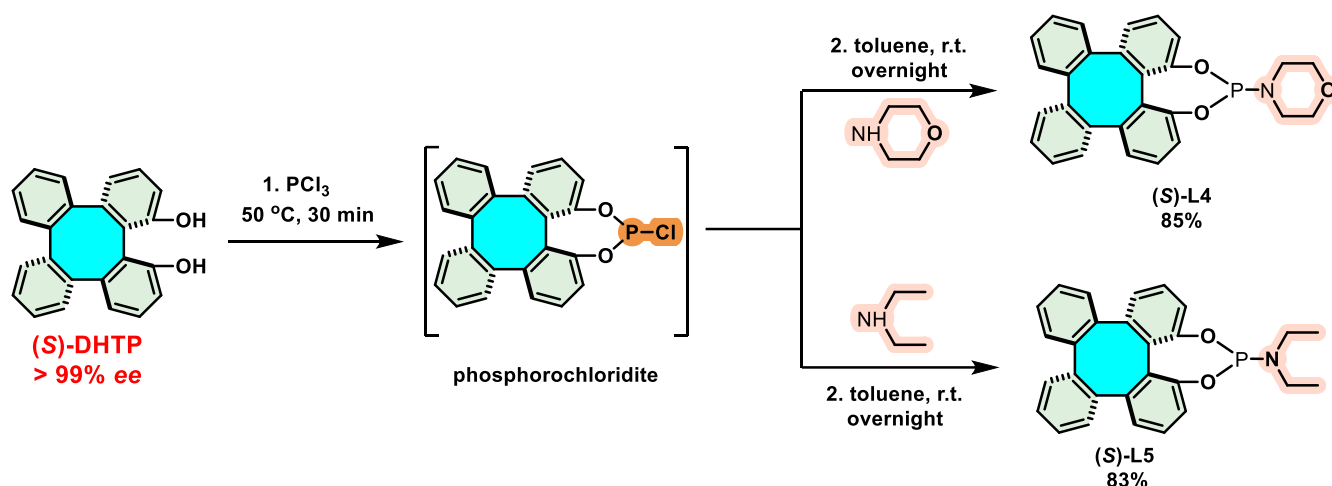
Procedure A:



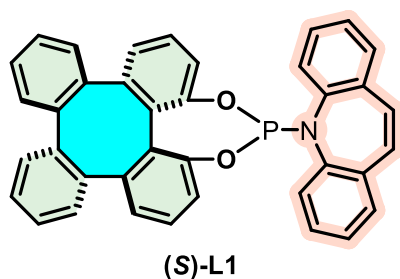
A flame dried Schlenk flask under argon was charged with the (*S*)-**DHTP** (1 mmol, 1.0 eq.) and PCl_3 (15.0 eq.) was heated at 50°C during 30 min. The initially heterogeneous mixture turned into a brownish homogenous solution. After cooling to room temperature (25°C), the excess PCl_3 was thoroughly evaporated in vacuo to remove remaining PCl_3 . The resulting phosphorochloridite was redissolved in anhydrous THF (5 mL). In a separate Schlenk flask under argon, the corresponding amine (1.2 eq.) dissolved in anhydrous THF (10 mL) was deprotonated at -78°C by the slow addition of *n*-BuLi (1.6 M solution in hexanes, 1.1 eq.). After being stirred at -78°C for 1 hour, the aforementioned phosphorochloridite solution was slowly transferred into the resulting solution via syringe. The resulting mixture was stirred at -78°C , then warmed to 25°C and continued to stir overnight. The solvent was evaporated in vacuo and purification by flash chromatography on silica gel using hexanes/toluene as the eluents to give the corresponding product as a white solid.

SUPPORTING INFORMATION

Procedure B:



A flame dried Schlenk flask under argon was charged with the (S)-DHTP (1 mmol, 1.0 eq.) and PCl_3 (15.0 eq.) was heated at 50 °C during 30 min. The initially heterogeneous mixture turned into a brownish homogenous solution. After cooling to room temperature (25 °C), the excess PCl_3 was thoroughly evaporated in vacuo to remove remaining PCl_3 . The resulting phosphorochloridite was dissolved in anhydrous toluene (5 mL) and cooled to 0 °C. To the resulting solution of phosphorochloridite were slowly added triethylamine (1.2 eq.) and the corresponding amine (1.2 eq.) via syringe. The resulting mixture was warmed to 25 °C and continued to stir overnight. The solvent was evaporated in vacuo and purification by flash chromatography on silica gel using hexanes/EtOAc as the eluents to give the corresponding product as a white solid.



This compound was prepared following general procedure A using iminostilbene.

White solid. 423.6 mg, 76% yield. mp 274.1 – 274.6 °C. $[\alpha]_{\text{D}}^{20}$: –225.00 ($c = 0.5$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 7.42 – 7.17 (m, 15H), 7.11 – 6.97 (m, 6H), 6.88 (dd, $J = 9.4, 8.0$ Hz, 2H), 6.76 (d, $J = 7.4$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, Acetone- d_6) δ 149.47, 149.07 (d, $J = 6.5$ Hz), 144.08 (d, $J = 1.6$ Hz), 143.01 (d, $J = 1.2$ Hz), 142.95, 142.77, 142.30 (d, $J = 4.4$ Hz), 141.27, 141.17, 141.03, 140.59, 136.45 (d, $J = 3.2$ Hz), 136.00, 131.60, 131.19, 130.43 (d, $J = 4.4$ Hz), 129.51, 129.40, 129.22, 129.21, 129.08 (d, $J = 3.0$ Hz),

SUPPORTING INFORMATION

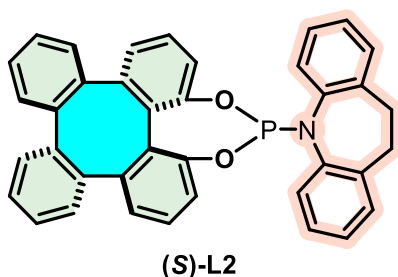
129.04, 128.98, 128.62, 128.59 (d, $J = 1.4$ Hz), 128.44 (d, $J = 8.4$ Hz), 128.26, 128.16, 127.82, 127.70, 127.30, 127.27, 126.91 (d, $J = 1.4$ Hz), 126.67, 126.65, 125.13, 120.67 (d, $J = 2.4$ Hz), 120.37.

DEPT 135 ^{13}C NMR (150 MHz, Acetone- d_6) δ 131.59, 131.19, 129.51, 129.40, 129.22, 129.21, 129.08 (d, $J = 2.8$ Hz), 129.05, 128.99, 128.62, 128.59, 128.44 (d, $J = 8.4$ Hz), 128.27, 128.16, 127.82, 127.70, 127.30, 127.27, 126.92, 126.67, 126.66, 125.13, 120.67 (d, $J = 2.5$ Hz), 120.37.

^{31}P NMR (162 MHz, Acetone- d_6) δ 135.09.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{38}\text{H}_{25}\text{NO}_2\text{P}]^+$ 558.1618, found 558.1625.

IR (neat): 3065, 1595, 1560, 1485, 1431, 1207, 1107, 1076, 991, 914, 800, 760, 748, 727, 629 cm^{-1} .



This compound was prepared following general procedure A using iminodibenzyl.

White solid. 403.2 mg, 72% yield. mp 270.1 – 270.6 °C. $[\alpha]_D^{20}$: -256.2 ($c = 0.5$, CHCl_3).

^1H NMR (400 MHz, CD_2Cl_2) δ 7.26 – 7.01 (m, 12H), 7.01 – 6.93 (m, 3H), 6.91 – 6.77 (m, 4H), 6.72 – 6.62 (m, 2H), 6.58 (d, $J = 8.0$ Hz, 1H), 3.55 (dddd, $J = 28.7, 15.2, 8.6, 3.2$ Hz, 2H), 2.87 – 2.73 (m, 2H).

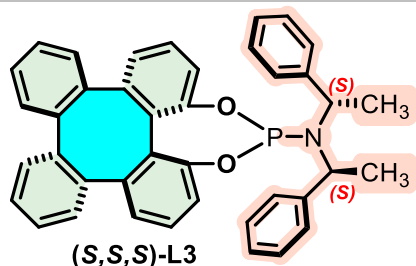
^{13}C NMR (100 MHz, CD_2Cl_2) δ 149.35, 149.26 (d, $J = 7.3$ Hz), 144.04 (d, $J = 1.5$ Hz), 143.13 (d, $J = 1.1$ Hz), 142.98 (d, $J = 16.3$ Hz), 142.82 (d, $J = 5.9$ Hz), 141.33, 141.25, 141.08, 140.71, 137.40 (d, $J = 3.4$ Hz), 137.29 (d, $J = 1.8$ Hz), 130.51 (d, $J = 4.6$ Hz), 130.21, 129.92, 129.71, 129.51, 129.02, 128.47 (d, $J = 1.5$ Hz), 128.42 (d, $J = 4.5$ Hz), 128.36, 128.30, 128.18 (d, $J = 2.2$ Hz), 127.87 (d, $J = 10.8$ Hz), 127.73, 127.34, 127.30, 127.11, 126.67, 126.53, 126.46, 126.40, 125.14, 120.91 (d, $J = 2.5$ Hz), 120.20, 31.62, 31.53.

^{31}P NMR (162 MHz, CD_2Cl_2) δ 133.79.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{38}\text{H}_{27}\text{NO}_2\text{P}]^+$ 560.1774, found 560.1785.

IR (neat): 3063, 2912, 1566, 1485, 1433, 1234, 1186, 1107, 984, 914, 798, 748, 725, 696, 629 cm^{-1} .

SUPPORTING INFORMATION



This compound was prepared following general procedure A using *bis*[(*S*)- α -methylbenzyl]amine.

White solid. 459.1 mg, 78% yield. mp 114.2 – 114.6 °C. $[\alpha]^{20}_{\text{D}}$: –430.1 ($c = 0.5$, CHCl₃).

$^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 7.41 – 7.32 (m, 3H), 7.31 – 7.10 (m, 16H), 7.07 – 7.02 (m, 2H), 7.01 – 6.94 (m, 2H), 6.85 (d, $J = 7.5$ Hz, 1H), 4.50 (dq, $J = 11.0, 7.0$ Hz, 2H), 1.68 (d, $J = 7.1$ Hz, 6H).

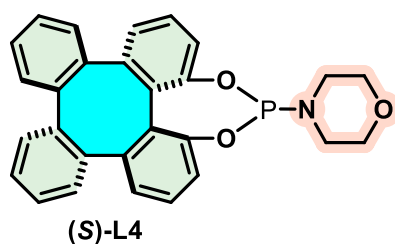
$^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 149.33, 149.04 (d, $J = 8.6$ Hz), 142.87 (d, $J = 1.6$ Hz), 142.47, 142.30, 140.35, 140.21, 140.18, 139.81, 129.57, 129.53, 128.75, 128.55, 127.72, 127.39 (d, $J = 1.8$ Hz), 127.22, 127.12, 127.04, 126.99, 126.97, 126.76, 126.53, 126.47, 126.03, 125.96, 125.66, 124.08, 119.91 (d, $J = 2.7$ Hz), 119.69, 53.72, 53.65, 21.98, 21.90.

Dept135 $^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 128.75, 128.55, 127.71, 127.22, 127.12, 127.04, 126.99, 126.97, 126.76, 126.53, 126.47, 126.03, 125.96, 125.66, 124.08, 119.91 (d, $J = 2.7$ Hz), 119.69, 53.72, 53.65, 21.98, 21.90.

$^{31}\text{P NMR}$ (243 MHz, CDCl₃) δ 149.30.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{40}\text{H}_{33}\text{NO}_2\text{P}]^+$ 590.2244, found 590.2254.

IR (neat): 3105, 2959, 2872, 1720, 1543, 1531, 1346, 1234, 1171, 1111, 1076, 910, 800, 752, 727, 700, 629 cm^{-1} .



This compound was prepared following general procedure A using morpholine.

White solid. 384.0 mg, 85% yield. mp 127.4 – 128.1 °C. $[\alpha]^{20}_{\text{D}}$: –149.5 ($c = 0.5$, CHCl₃).

$^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 7.41 – 7.28 (m, 6H), 7.24 (dd, $J = 7.5, 1.3$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.13 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 2H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 3.51 (t, $J = 4.7$ Hz, 4H), 3.14 – 3.03 (m, 2H), 3.00 – 2.89 (m, 2H).

SUPPORTING INFORMATION

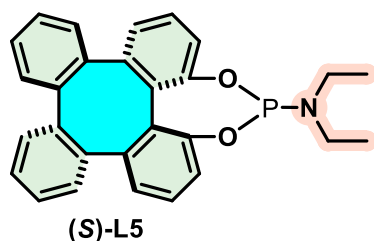
^{13}C NMR (100 MHz, Acetone- d_6) δ 150.03, 149.61 (d, $J = 4.4$ Hz), 143.96 (d, $J = 1.7$ Hz), 143.64, 141.21, 141.14, 140.92, 140.67, 130.38 (d, $J = 4.2$ Hz), 129.55, 129.40 (d, $J = 1.8$ Hz), 129.09, 129.07, 128.49, 128.47, 127.83, 127.80, 127.38, 127.33, 126.56 (d, $J = 1.6$ Hz), 125.64, 120.64, 120.47 (d, $J = 2.2$ Hz), 67.48, 67.43, 44.45, 44.27.

Dept135 ^{13}C NMR (150 MHz, Acetone- d_6) δ 129.55, 129.09, 129.06, 128.49, 128.47, 127.83, 127.80, 127.38, 127.33, 126.56, 125.63, 120.64, 120.47 (d, $J = 2.1$ Hz), 67.47, 67.44, 44.42, 44.30.

^{31}P NMR (162 MHz, Acetone- d_6) δ 141.99.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{28}\text{H}_{23}\text{NO}_3\text{P}]^+$ 452.1411, found 452.1417.

IR (neat): 3107, 2957, 2928, 2855, 1720, 1543, 1431, 1346, 1258, 1234, 1171, 1111, 1078, 1043, 954, 910, 800, 761, 744, 727, 700, 679, 630 cm^{-1} .



This compound was prepared following general procedure B using diethylamine.

White solid. 363.5 mg, 83% yield. mp 95.4 – 95.8 °C. $[\alpha]_D^{20}$: -217.1 ($c = 0.5$, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.20 (m, 2H), 7.20 – 7.08 (m, 6H), 7.06 – 6.96 (m, 3H), 6.87 (tdd, $J = 7.7, 6.6, 1.2$ Hz, 3H), 3.02 – 2.87 (m, 2H), 2.75 (ddd, $J = 14.3, 12.9, 7.0$ Hz, 2H), 0.98 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.19, 149.90 (d, $J = 4.2$ Hz), 143.73 (d, $J = 1.4$ Hz), 143.50, 141.25, 141.16, 141.14, 140.88, 130.47 (d, $J = 4.3$ Hz), 129.84, 129.66, 129.43 (d, $J = 1.8$ Hz), 128.65, 128.54, 128.49, 128.40, 127.53, 127.13, 127.07, 126.49 (d, $J = 1.4$ Hz), 125.34, 120.59 (d, $J = 2.4$ Hz), 120.19, 38.37, 38.15, 14.82, 14.79.

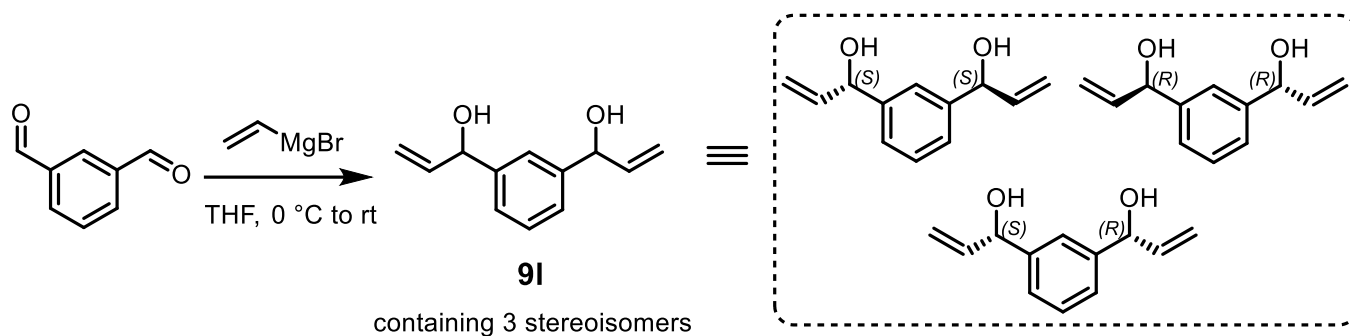
^{31}P NMR (162 MHz, CDCl_3) δ 147.00.

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{28}\text{H}_{25}\text{NO}_2\text{P}]^+$ 438.1618, found 438.1624.

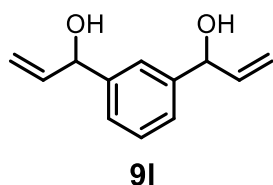
IR (neat): 3107, 2961, 2910, 2872, 1719, 1630, 1541, 1462, 1346, 1277, 1169, 1078, 1041, 995, 916, 798, 727, 719, 680, 630 cm^{-1} .

SUPPORTING INFORMATION

Procedure for the Synthesis of **91** ^[1]



In a flame dried Schlenk flask, a solution of isophthalaldehyde (10 mmol, 1.34 g) in dry THF (20 mL) was cooled to 0 °C under Argon. Vinyl magnesium bromide (20 mmol, 20 ml, 1.0 M in THF) was added dropwise. After 15 min, the reaction was allowed to warm to room temperature and stirred for additional 3 h. The reaction mixture was quenched by addition of saturated aqueous NH₄Cl and extracted with EtOAc (3×50 ml). The organic phase was washed with brine, dried over MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (EtOAc/hexane 1:4) to give the corresponding allylic alcohol substrates **91** (containing 3 stereoisomers which were not separable by TLC and NMR).



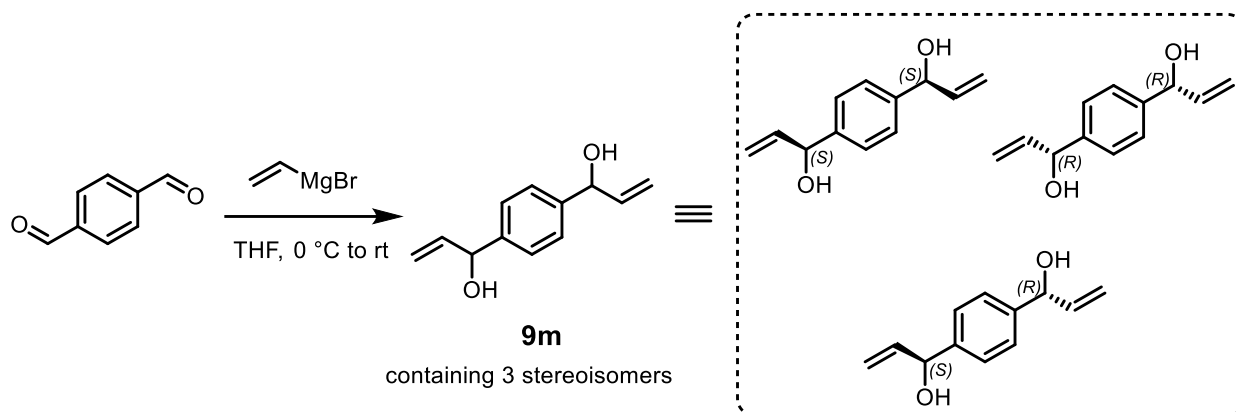
Colorless oil. 1.05 g, 55% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.29 (s, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.01 – 5.87 (m, 2H), 5.30 – 5.20 (m, 2H), 5.14 – 5.05 (m, 4H), 2.32 (s, 2H).

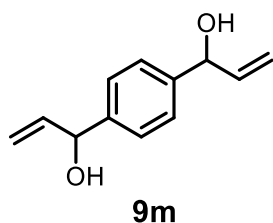
¹³C NMR (100 MHz, CDCl₃) δ 142.95, 140.10, 128.76, 125.78, 124.28, 115.28, 75.26.

SUPPORTING INFORMATION

Procedure for the Synthesis of **9m** ^[2]



In a flame dried Schlenk flask, a solution of terephthalaldehyde (10 mmol, 1.34 g) in dry THF (20 mL) was cooled to 0 °C under Argon. Vinyl magnesium bromide (20 mmol, 20 ml, 1.0 M in THF) was added dropwise. After 15 min, the reaction was allowed to warm to room temperature and stirred for additional 3 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc (3×50 ml). The organic phase was washed with brine, dried over MgSO_4 . The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (EtOAc/hexane 1:4) to give the corresponding allylic alcohol substrates **9m** (containing 3 stereoisomers which were not separable by TLC and NMR).



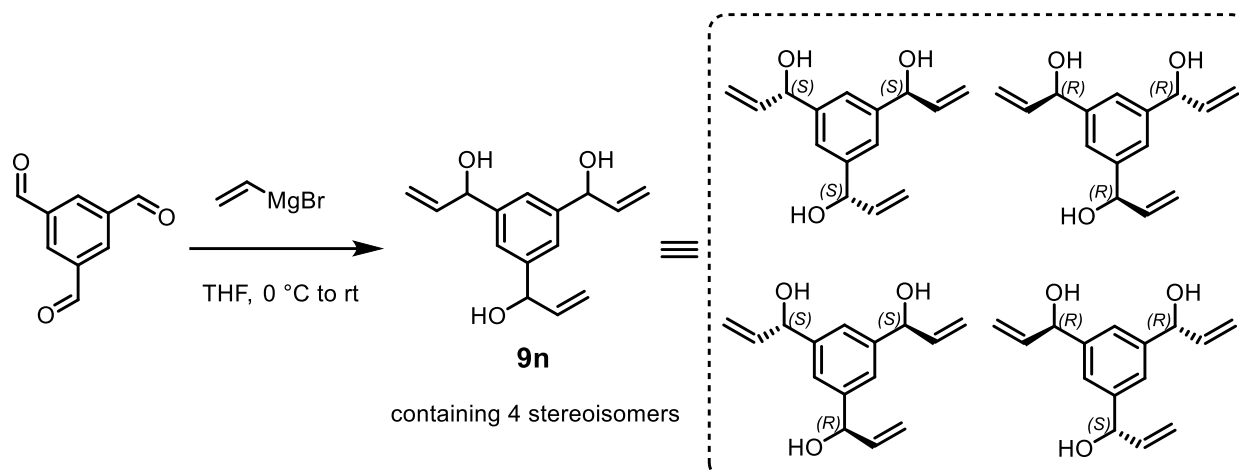
White solid. 0.80 g, 42% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (s, 4H), 6.04 – 5.87 (m, 2H), 5.28 (d, $J = 17.1$ Hz, 2H), 5.18 – 5.08 (m, 4H), 1.86 (brs, 2H).

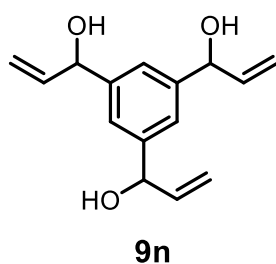
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.13, 140.14, 126.56, 115.24, 75.13.

SUPPORTING INFORMATION

Procedure for the Synthesis of **9n**



In a flame dried Schlenk flask, a solution of benzene-1,3,5-tricarbaldehyde (10 mmol, 1.62 g) in dry THF (20 mL) was cooled to $0\text{ }^\circ\text{C}$ under Argon. Vinyl magnesium bromide (30 mmol, 30 mL, 1.0 M in THF) was added dropwise. After 15 min, the reaction was allowed to warm to room temperature and stirred for additional 3 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc (3×50 mL). The organic phase was washed with brine, dried over MgSO_4 . The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (EtOAc/hexane 1:2) to give the corresponding allylic alcohol substrates **9n** (containing 4 stereoisomers which were not separable by TLC and NMR).



Pale yellow solid. 1.16 g, 47% yield. mp $97.9 - 98.5\text{ }^\circ\text{C}$.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 7.16 (s, 1H), 5.91 (ddd, $J = 16.5, 10.0, 6.0$ Hz, 1H), 5.45 (d, $J = 3.9$ Hz, 1H), 5.24 (d, $J = 17.1$ Hz, 1H), 5.10 – 4.95 (m, 2H).

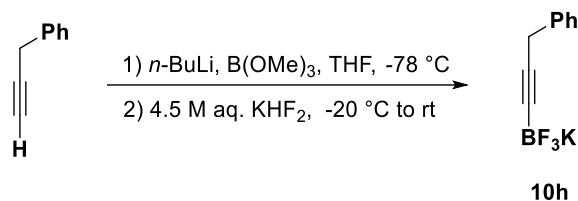
$^{13}\text{C NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ 144.30, 142.51, 123.14, 113.78, 74.09.

HRMS (ESI): $[\text{M}+\text{Na}]^+$ Calcd for $[\text{C}_{15}\text{H}_{18}\text{O}_3\text{Na}]^+$ 269.1149, found 269.1143.

IR(neat): 3367, 2922, 2855, 1660, 1603, 1470, 1421, 1221, 991, 912, 773, 745, 611 cm^{-1} .

SUPPORTING INFORMATION

Procedure for the Synthesis of Potassium Alkynyltrifluoroborates **10h** [3]



To a solution of 3-phenyl-1-propyne (5 mmol, 0.58 g) in dry THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (5 mmol, 3.1 mL, 1.6 M in hexane) was added dropwise. The resulting solution was stirred for 0.5 h. Trimethylborate (7.5 mmol, 0.78 g) was added dropwise at $-78\text{ }^{\circ}\text{C}$. After being stirred for 0.5 h, the reaction mixture was warmed to $-20\text{ }^{\circ}\text{C}$ and stirred for additional 0.5 h. Aqueous KHF_2 (30 mmol) was added dropwise, and after 1 h the solution was allowed to warm to rt for 2 h. The solvent was removed under reduced pressure. The residue was dried under vacuum to remove water and then dissolved in hot acetone (3 x 15 mL). The solution was filtered and the filtrate was concentrated to a minimal volume (~ 10 mL) under vacuum. Et_2O (~ 30 mL) was added to precipitate the potassium trifluoroborate. The mixture was cooled to $0\text{ }^{\circ}\text{C}$ to complete the precipitation. The white solid was collected by filtration to give **10h**.



White solid. 0.61 g, 55% yield.

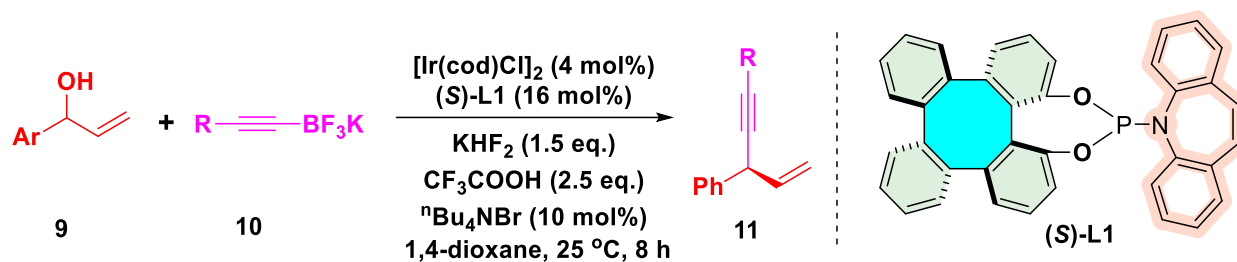
$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.35 – 7.27 (m, 4H), 7.22 – 7.17 (m, 1H), 3.44 (s, 2H).

$^{13}\text{C NMR}$ (150 MHz, $\text{DMSO-}d_6$) δ 138.69, 128.64, 128.32, 126.52, 87.00 (relaxation time $d_1 = 3$ seconds, no clear signal for the second acetylenic carbon atom), 25.57.

$^{19}\text{F NMR}$ (565 MHz, $\text{DMSO-}d_6$) δ -131.25.

HRMS (ESI): $[\text{M-K}]^-$ Calcd for $[\text{C}_9\text{H}_7\text{BF}_3]^-$ 183.0598, found 183.0591.

General Procedure for Ir-Catalyzed Allylic Alkynylation



A) Procedure for Product 11a:

$[\text{Ir}(\text{cod})\text{Cl}]_2$ (5.4 mg, 8.0 μmol , 4 mol%) and (S)-L1 (17.8 mg, 32.0 μmol , 16 mol%) were dissolved in 1,4-dioxane (0.4 mL) in a Schlenk tube and vigorously stirred for 15 min. To the resulting dark red solution, allylic alcohol **9a** (0.2 mmol, 1.0 eq.), potassium alkynyltrifluoroborate **10a** (0.3 mmol, 1.5 eq.), $n\text{Bu}_4\text{NBr}$ (6.6 mg, 20 μmol , 10 mol%), KHF_2 (23.7 mg, 0.3 mmol, 1.5 eq.), and CF_3COOH (58.0 mg, 0.5 mmol, 2.5 eq.) were sequentially added. Reaction vessel was flushed with nitrogen, and resulting heterogeneous orange mixture was stirred at 25 °C for 8 h. The reaction mixture was diluted with hexanes (1.0 mL), treated with triethylamine (0.1 mL), and directly subjected to purification by flash chromatography on silica gel using CH_2Cl_2 /hexane as the eluents to give the product **11a**.

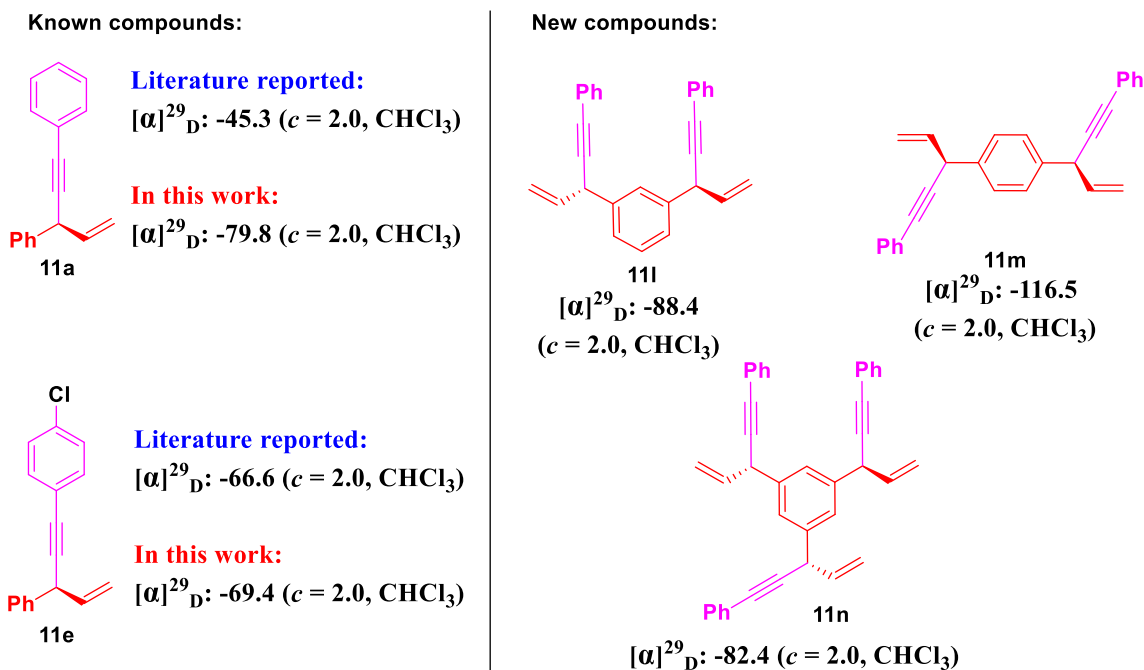
B) General Procedure for Products 11b-n:

$[\text{Ir}(\text{cod})\text{Cl}]_2$ (10.8 mg, 16.0 μmol , 4 mol%) and (S)-L1 (35.6 mg, 64.0 μmol , 16 mol%) were dissolved in 1,4-dioxane (0.8 mL) in a Schlenk tube and vigorously stirred for 15 min. To the resulting dark red solution, allylic alcohol **9** (0.4 mmol, 1.0 eq.), potassium alkynyltrifluoroborate **10** (0.6 mmol, 1.5 eq.), $n\text{Bu}_4\text{NBr}$ (13.0 mg, 40 μmol , 10 mol%), KHF_2 (47.6 mg, 0.6 mmol, 1.5 eq.), and CF_3COOH (115.2 mg, 1.0 mmol, 2.5 eq.) were sequentially added. Reaction vessel was flushed with nitrogen, and resulting heterogeneous orange mixture was stirred at 25 °C for 8 h. The reaction mixture was diluted with hexanes (2.0 mL), treated with triethylamine (0.2 mL), and directly subjected to purification by flash chromatography on silica gel using CH_2Cl_2 /hexane as the eluents to give the product **11**.

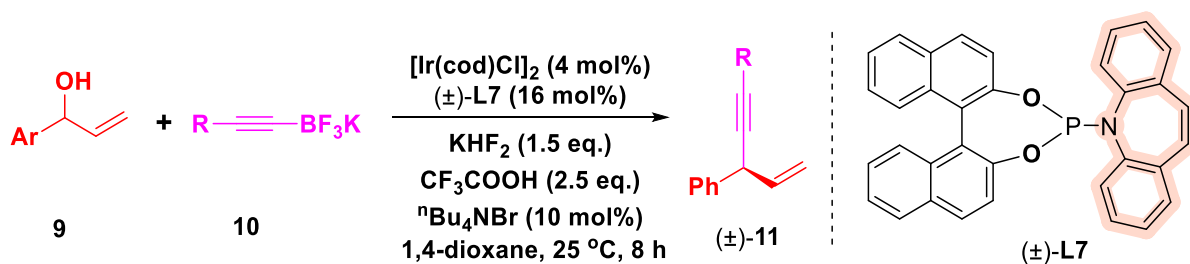
(Notes: when the substrate **9** containing two or three allylic alcohol moieties (**9l**, **9m** and **9n**), the usage amount of potassium alkynyltrifluoroborate **10** and all of additives were double or triple, respectively.)

SUPPORTING INFORMATION

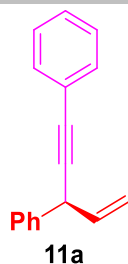
The stereoconfiguration of products **11a-n** was determined by comparison of optical rotations of **11a** and **11e** previously reported in literature (*Angew. Chem. Int. Ed.*, **2013**, *52*, 7532-7535).^[4]



The (\pm)-**11a-n** for HPLC determination were prepared by using racemic BINOL-based (\pm)-**L7** as a ligand under the above standard conditions.



SUPPORTING INFORMATION



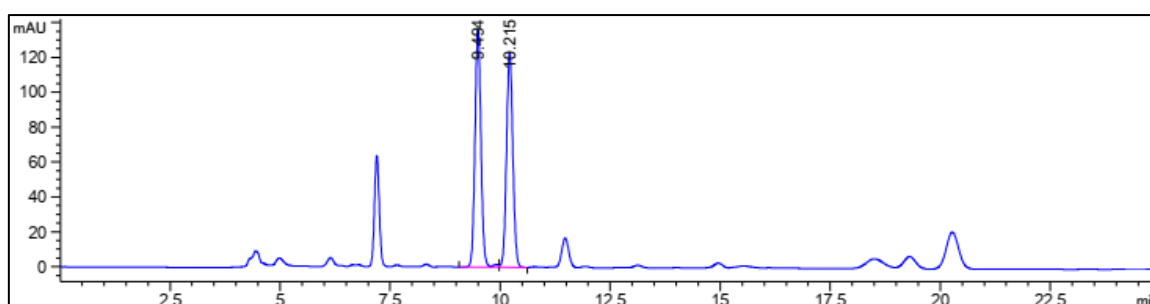
Colorless oil. 37.1 mg, 85% yield. $[\alpha]_{\text{D}}^{29}$: -79.8 ($c = 2.0$, CHCl_3) (lit^[4]: $[\alpha]_{\text{D}}^{29}$: -45.3 ($c = 2.0$, CHCl_3)).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 – 7.40 (m, 4H), 7.39 – 7.32 (m, 2H), 7.32 – 7.28 (m, 3H), 7.27 – 7.24 (m, 1H), 6.01 (ddd, $J = 16.9, 9.9, 6.1$ Hz, 1H), 5.46 (dt, $J = 16.9, 1.5$ Hz, 1H), 5.19 (dt, $J = 9.9, 1.4$ Hz, 1H), 4.59 (d, $J = 6.1$ Hz, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 140.15, 137.91, 131.67, 128.65, 128.22, 127.96, 127.68, 127.02, 123.49, 115.25, 88.64, 85.32, 41.96.

HPLC: Daicel Chiralcel® OJ-H, 5% $i\text{PrOH}$, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (t_{R} (major) = 9.27 min, t_{R} (minor) = 10.00 min).

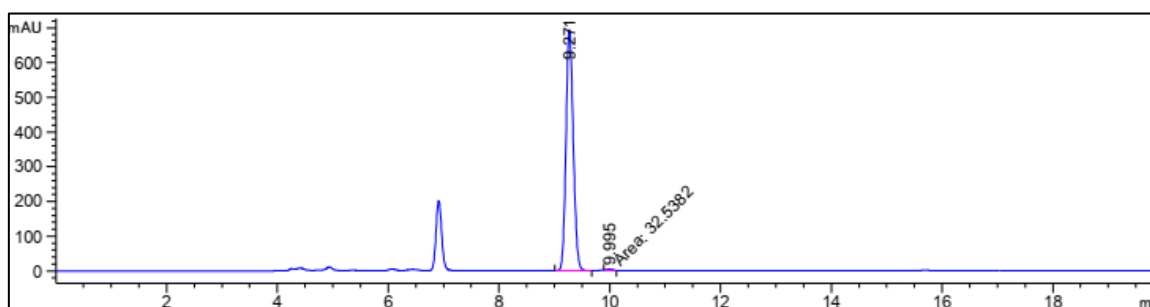
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.494	BV R	0.1456	1288.26501	135.75891	51.0988
2	10.215	VB	0.1566	1232.85950	123.40372	48.9012

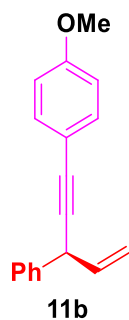
Totals : 2521.12451 259.16264

Enantioenriched



SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.271	BB	0.1423	6316.11670	693.52704	99.4875
2	9.995	MM	0.1433	32.53820	3.78506	0.5125
Totals :				6348.65490	697.31210	



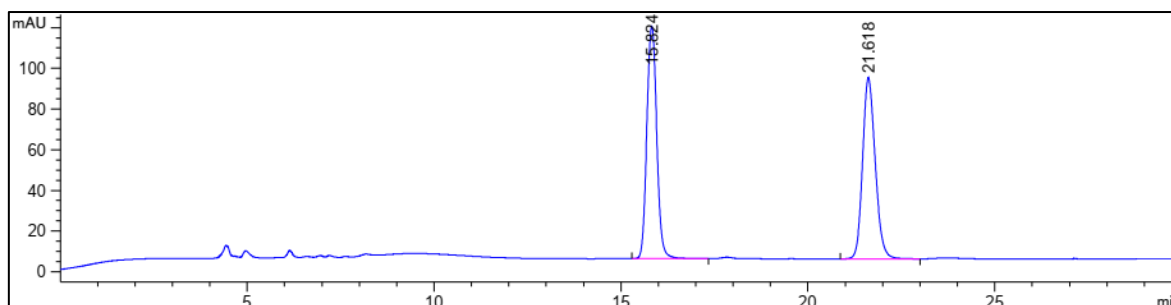
Colorless oil. 80.4 mg, 81% yield.

¹H NMR (600 MHz, CDCl₃) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.00 (ddd, *J* = 16.4, 9.9, 6.1 Hz, 1H), 5.44 (d, *J* = 16.9 Hz, 1H), 5.17 (d, *J* = 9.8 Hz, 1H), 4.57 (d, *J* = 6.2 Hz, 1H), 3.80 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.37, 140.37, 138.14, 133.05, 128.63, 127.69, 126.97, 115.65, 115.13, 113.85, 87.10, 85.13, 55.29, 42.01.

HPLC: Daicel Chiralcel® OJ-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 96% *ee* (*t_R* (major) = 16.95 min, *t_R* (minor) = 23.73 min).

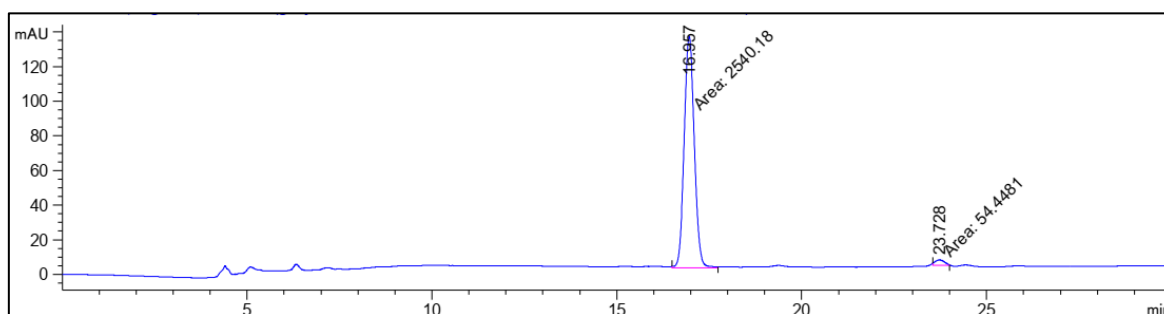
Racemic



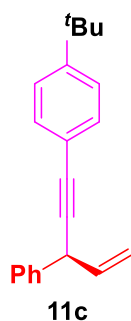
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.824	BB	0.2909	2102.51221	114.13593	50.0980
2	21.618	BB	0.3599	2094.28369	89.21770	49.9020
Totals :				4196.79590	203.35363	

SUPPORTING INFORMATION

Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.957	MM	0.3170	2540.18237	133.55299	97.9015
2	23.728	MM	0.2965	54.44814	3.06016	2.0985
Totals :				2594.63051	136.61316	



Colorless oil. 76.8 mg, 70% yield.

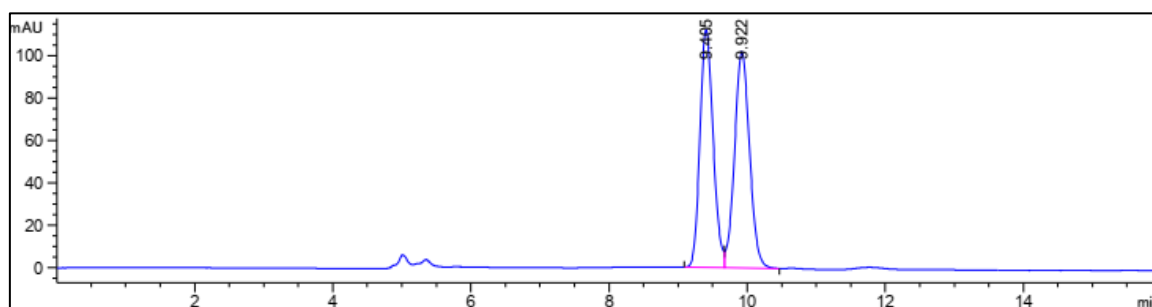
¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.41 (m, 4H), 7.41 – 7.33 (m, 4H), 7.32 – 7.26 (m, 1H), 6.03 (ddd, *J* = 16.8, 9.9, 6.1 Hz, 1H), 5.48 (dt, *J* = 16.9, 1.4 Hz, 1H), 5.21 (dt, *J* = 9.9, 1.4 Hz, 1H), 4.61 (d, *J* = 6.0 Hz, 1H), 1.34 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 151.20, 140.31, 138.08, 131.40, 128.64, 127.70, 126.98, 125.24, 120.49, 115.15, 87.91, 85.43, 42.01, 34.74, 31.21.

HPLC: Daicel Chiralcel® OJ-H, 0.5% *i*PrOH, 99.5% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (*t*_R (major) = 9.98 min, *t*_R(minor) = 9.60 min).

SUPPORTING INFORMATION

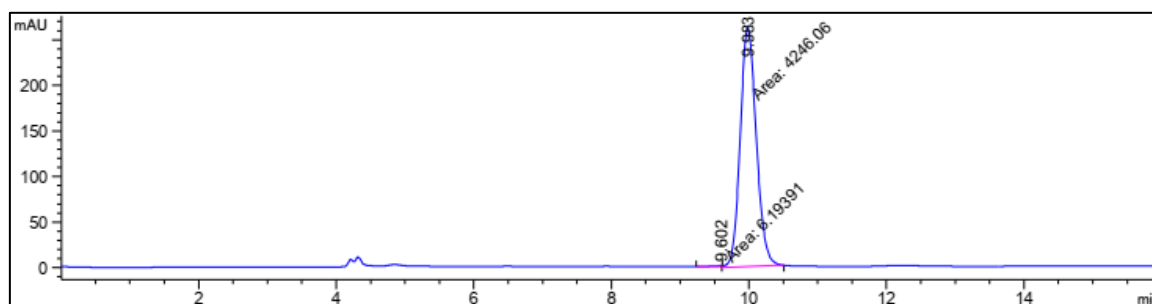
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.405	BV	0.2071	1488.04211	111.96686	49.0649
2	9.922	VB	0.2326	1544.76270	102.03087	50.9351

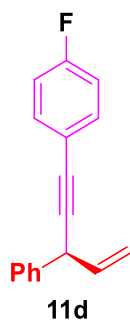
Totals : 3032.80481 213.99773

Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.602	MM	0.1278	6.19391	8.07729e-1	0.1457
2	9.983	MM	0.2699	4246.05811	262.18356	99.8543

Totals : 4252.25202 262.99129



Colorless oil. 70.8 mg, 75% yield. $[\alpha]_D^{29}$: -43.7 ($c = 2.0$, CHCl_3).

SUPPORTING INFORMATION

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.39 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.30 – 7.23 (m, 1H), 6.99 (t, $J = 8.7$ Hz, 2H), 5.99 (ddd, $J = 16.9, 9.9, 6.1$ Hz, 1H), 5.44 (dt, $J = 16.9, 1.5$ Hz, 1H), 5.19 (dt, $J = 9.8, 1.4$ Hz, 1H), 4.57 (d, $J = 6.1$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.34 (d, $J = 248.8$ Hz), 140.04, 137.80, 133.52 (d, $J = 8.3$ Hz), 128.71, 127.67, 127.10, 119.53 (d, $J = 3.6$ Hz), 115.59, 115.36 (d, $J = 3.3$ Hz), 88.33, 84.23, 41.92.

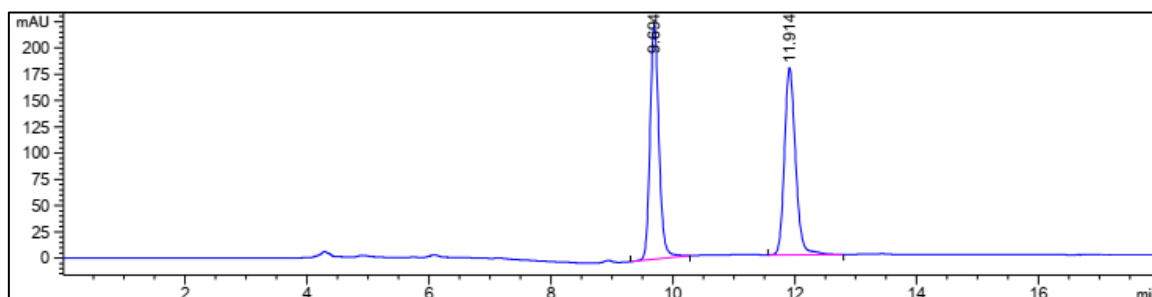
^{19}F NMR (376 MHz, CDCl_3) δ -111.59.

HRMS (APCI): $[\text{M}]^+$ Calcd. for $[\text{C}_{17}\text{H}_{13}\text{F}]^+$ 236.0996, found 236.1000.

IR (neat): 3065, 3020, 2978, 2203, 1599, 1506, 1452, 1215, 1155, 837, 752, 698, 667 cm^{-1} .

HPLC: Daicel Chiralcel[®] OJ-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (t_{R} (major) = 9.56 min, t_{R} (minor) = 11.75 min).

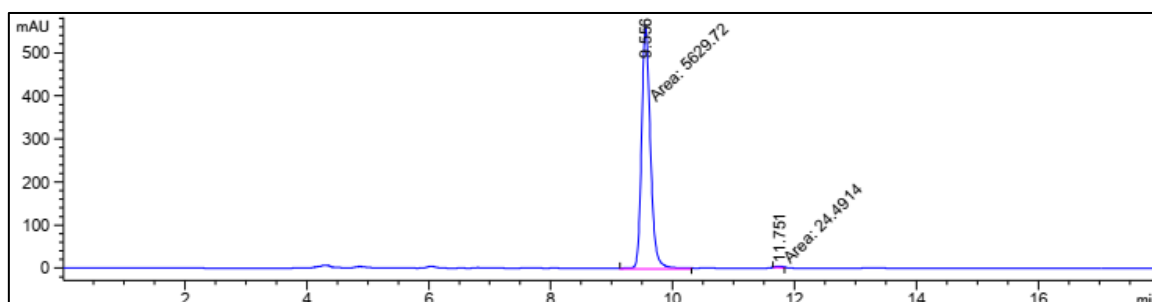
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.694	BB	0.1560	2260.02466	223.42888	50.1592
2	11.914	BB	0.1935	2245.67603	177.66737	49.8408

Totals : 4505.70068 401.09625

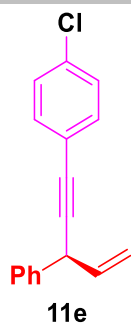
Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.556	MM	0.1684	5629.71973	557.02747	99.5668
2	11.751	MM	0.1328	24.49144	3.07461	0.4332

Totals : 5654.21117 560.10208

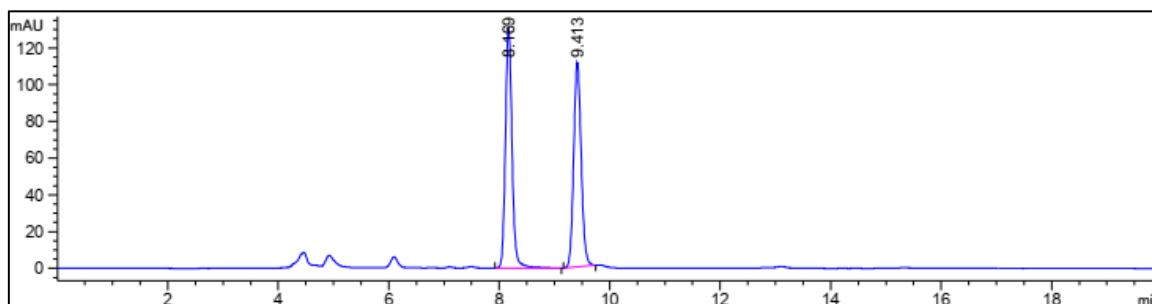
SUPPORTING INFORMATION



Colorless oil. 66.5 mg, 66% yield. $[\alpha]_D^{29}$: -69.4 ($c = 2.0$, CHCl_3) (lit^[4]: $[\alpha]_D^{29}$: -66.6 ($c = 2.0$, CHCl_3)).
 ^{13}C NMR (150 MHz, CDCl_3) δ 139.91, 137.67, 133.97, 132.92, 128.72, 128.57, 127.66, 127.14, 121.98, 115.42, 89.75, 84.20, 41.96.

HPLC: Daicel Chiralcel[®] OJ-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 8.20 min, t_R (minor) = 9.47 min).

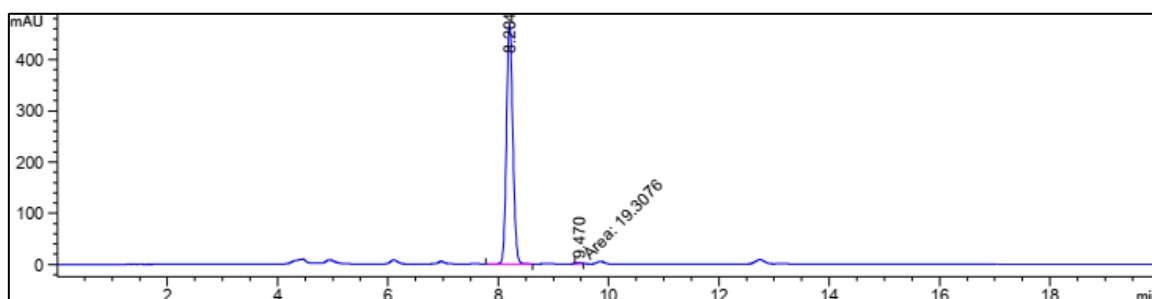
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.169	BB	0.1271	1087.18237	130.65259	50.9298
2	9.413	BB	0.1456	1047.48816	111.48887	49.0702

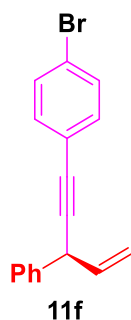
Totals : 2134.67053 242.14146

Enantioenriched



SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.204	BB	0.1225	3720.83691	469.10587	99.4838
2	9.470	MM	0.1208	19.30764	2.66430	0.5162
Totals :				3740.14455	471.77017	



Colorless oil. 61.6 mg, 52% yield. $[\alpha]_D^{29}$: -38.3 ($c = 2.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 – 7.39 (m, 4H), 7.38 – 7.24 (m, 5H), 5.99 (ddd, $J = 16.9, 9.8, 6.1$ Hz, 1H), 5.43 (dt, $J = 16.9, 1.4$ Hz, 1H), 5.19 (dt, $J = 9.8, 1.4$ Hz, 1H), 4.56 (d, $J = 6.1$ Hz, 1H).

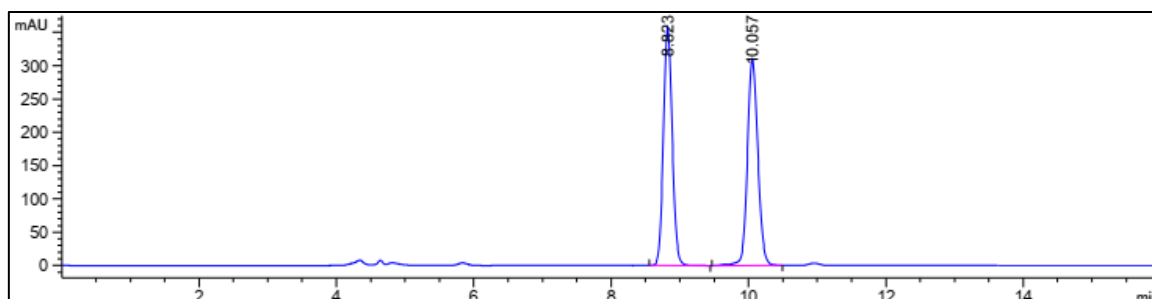
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.87, 137.63, 133.15, 131.50, 128.73, 127.67, 127.15, 122.45, 122.16, 115.44, 89.96, 84.26, 41.98.

HRMS (APCI): $[\text{M}]^+$ Calcd. for $[\text{C}_{17}\text{H}_{13}\text{Br}]^+$ 296.0196, found 296.0200.

IR (neat): 3063, 3020, 2928, 2203, 1639, 1585, 1485, 1215, 1070, 1011, 926, 825, 748, 698, 667 cm^{-1} .

HPLC: Daicel Chiralcel® OJ-H, 5% i PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 8.82 min, t_R (minor) = 10.09 min).

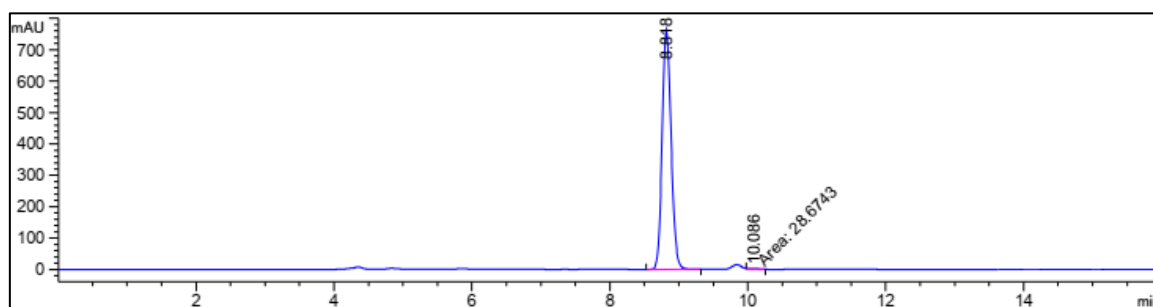
Racemic



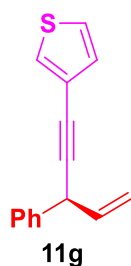
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.823	BB	0.1382	3194.30542	357.58911	49.3361
2	10.057	BB	0.1633	3280.27783	310.31012	50.6639
Totals :				6474.58325	667.89923	

SUPPORTING INFORMATION

Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.818	BB	0.1395	6907.74609	764.23743	99.5866
2	10.086	MM	0.1728	28.67433	2.76591	0.4134
Totals :				6936.42042	767.00334	



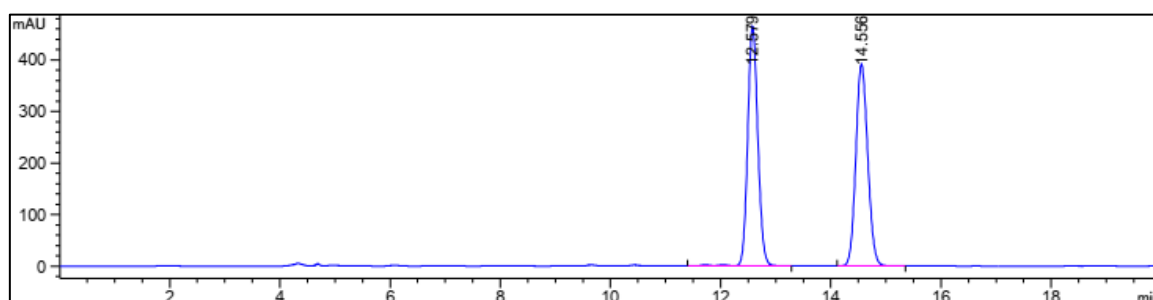
Colorless oil. 62.7 mg, 70% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 – 7.38 (m, 3H), 7.39 – 7.30 (m, 2H), 7.29 – 7.21 (m, 2H), 7.12 (dd, $J = 5.0, 1.2$ Hz, 1H), 5.99 (ddd, $J = 16.9, 9.9, 6.1$ Hz, 1H), 5.43 (dt, $J = 16.9, 1.5$ Hz, 1H), 5.18 (dt, $J = 9.9, 1.4$ Hz, 1H), 4.56 (d, $J = 6.1$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.09, 137.86, 130.06, 128.69, 128.26, 127.71, 127.07, 125.14, 122.46, 115.34, 88.21, 80.36, 42.01.

HPLC: Daicel Chiralcel[®] OJ-H, 5% i PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 97% *ee* (t_{R} (major) = 12.58 min, t_{R} (minor) = 14.61 min).

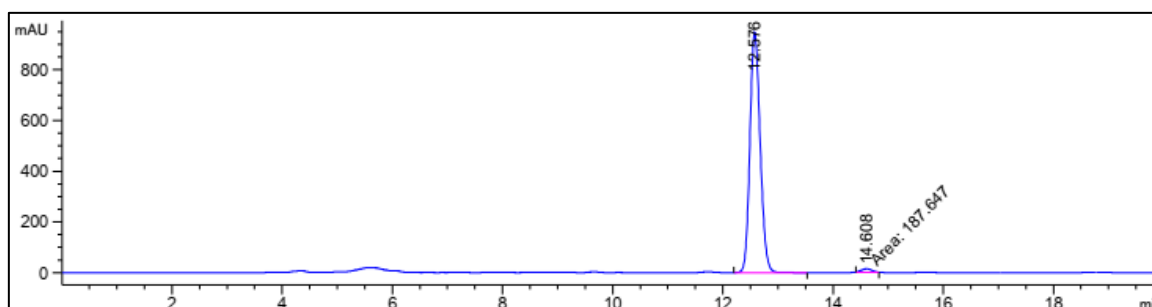
Racemic



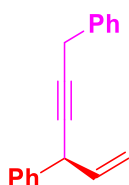
SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.579	VB R	0.1962	5956.21240	464.37054	50.3978
2	14.556	BB	0.2326	5862.19141	391.59781	49.6022
Totals :				1.18184e4	855.96835	

Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.576	BB	0.2008	1.22444e4	947.32043	98.4906
2	14.608	MM	0.2237	187.64713	13.98213	1.5094
Totals :				1.24320e4	961.30256	



11h

Colorless oil. 30.6 mg, 33% yield. $[\alpha]_D^{29}$: -19.8 ($c = 2.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.28 (m, 8H), 7.27 – 7.19 (m, 2H), 5.95 (ddd, $J = 16.6, 9.9, 6.1$ Hz, 1H), 5.39 (dt, $J = 16.8, 1.6$ Hz, 1H), 5.13 (dt, $J = 9.9, 1.5$ Hz, 1H), 4.42 (dd, $J = 4.1, 2.0$ Hz, 1H), 3.70 (d, $J = 2.3$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.59, 138.42, 137.19, 128.60, 128.49, 127.90, 127.65, 126.91, 126.51, 114.97, 82.84, 81.43, 41.60, 25.31.

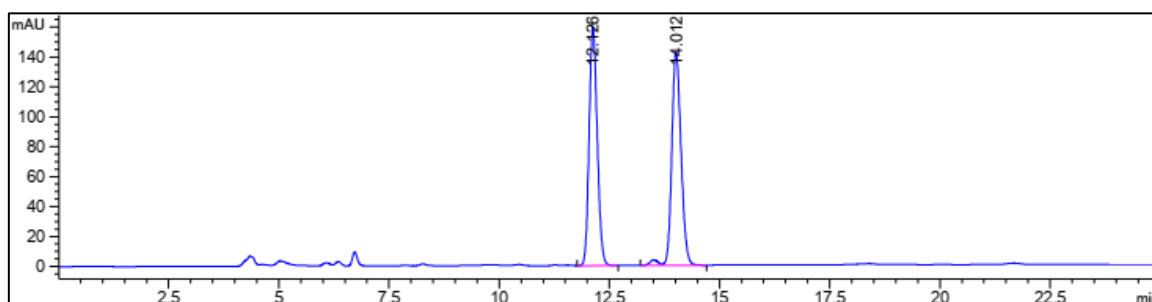
HRMS (APCI): $[\text{M}]^+$ Calcd. for $[\text{C}_{18}\text{H}_{16}]^+$ 232.1247, found 232.1252.

IR (neat): 3063, 3032, 2922, 2237, 1730, 1643, 1599, 1493, 1452, 1269, 1208, 923, 756, 733, 698 cm^{-1} .

HPLC: Daicel Chiralcel[®] OJ-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 14.38 min, t_R (minor) = 12.44 min).

SUPPORTING INFORMATION

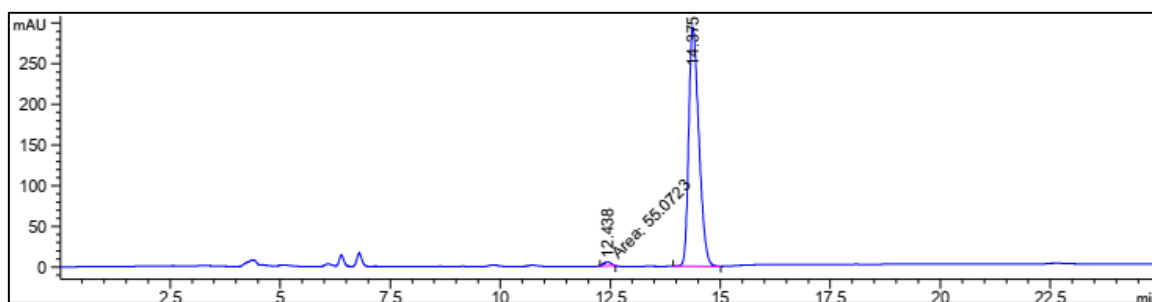
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.126	BB	0.1993	2041.53931	159.48875	49.1826
2	14.012	VB R	0.2245	2109.39917	142.68480	50.8174

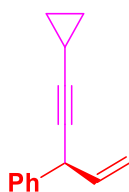
Totals : 4150.93848 302.17355

Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.438	MM	0.1861	55.07228	4.93144	1.1561
2	14.375	BB	0.2472	4708.69580	293.51111	98.8439

Totals : 4763.76808 298.44255



11i

Colorless oil. 50.2 mg, 69% yield.

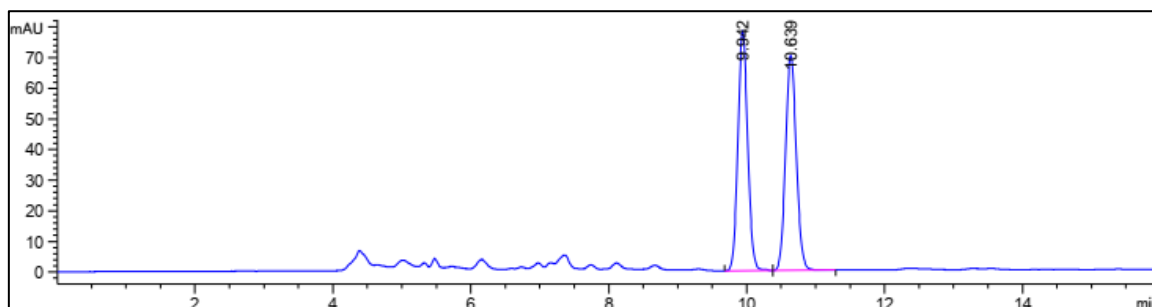
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.27 (m, 4H), 7.26 – 7.18 (m, 1H), 5.89 (ddd, $J = 16.9, 9.9, 6.2$ Hz, 1H), 5.32 (dt, $J = 16.9, 1.5$ Hz, 1H), 5.10 (dt, $J = 9.8, 1.5$ Hz, 1H), 4.30 (dd, $J = 6.1, 1.8$ Hz, 1H), 1.35 – 1.25 (m, 1H), 0.80 – 0.71 (m, 2H), 0.73 – 0.65 (m, 2H).

SUPPORTING INFORMATION

^{13}C NMR (100 MHz, CDCl_3) δ 141.01, 138.92, 128.81, 127.86, 127.09, 114.98, 88.83, 74.54, 41.75, 8.54, 8.52.

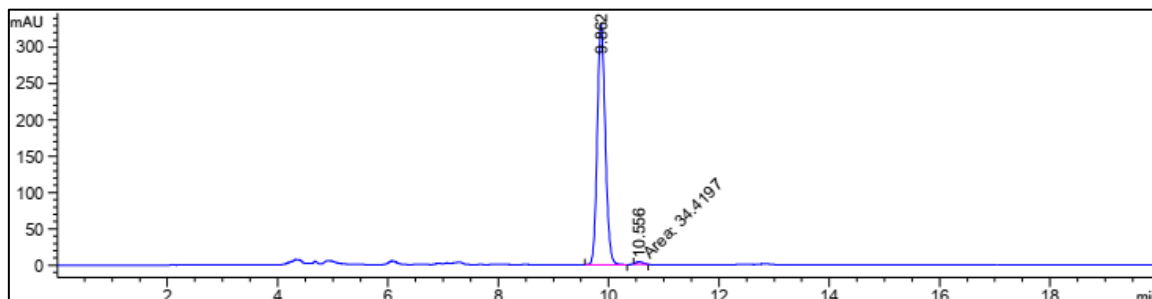
HPLC: Daicel Chiralcel[®] OJ-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 98% *ee* (t_{R} (major) = 9.86 min, t_{R} (minor) = 10.56 min).

Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.942	BB	0.1533	772.03949	78.09308	50.3387
2	10.639	BB	0.1685	761.65063	70.23734	49.6613
Totals :				1533.69012	148.33042	

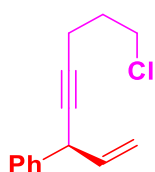
Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.862	BB	0.1553	3326.27954	330.72723	98.9758
2	10.556	MM	0.1571	34.41967	3.65092	1.0242
Totals :				3360.69921	334.37815	

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.980	MM	0.1980	13.99014	1.17753	0.2968
2	14.419	MM	0.2964	4699.84814	264.25183	99.7032
Totals :				4713.83828	265.42937	



11k

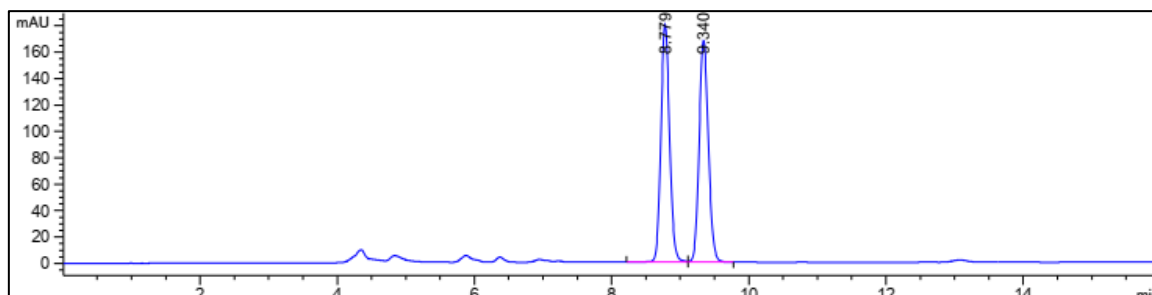
Colorless oil. 33.1 mg, 38% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.29 (m, 4H), 7.27 – 7.21 (m, 1H), 5.91 (ddd, $J = 16.9, 9.9, 6.1$ Hz, 1H), 5.34 (dt, $J = 16.8, 1.5$ Hz, 1H), 5.12 (dt, $J = 9.8, 1.4$ Hz, 1H), 4.38 – 4.28 (m, 1H), 3.66 (t, $J = 6.4$ Hz, 2H), 2.47 (td, $J = 6.8, 2.3$ Hz, 2H), 1.99 (p, $J = 6.6$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.55, 138.42, 128.60, 127.54, 126.92, 114.84, 83.37, 80.24, 43.79, 41.46, 31.65, 16.39.

HPLC: Daicel Chiralcel[®] OJ-H, 5% *i*PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (t_{R} (major) = 9.39 min, t_{R} (minor) = 8.82 min).

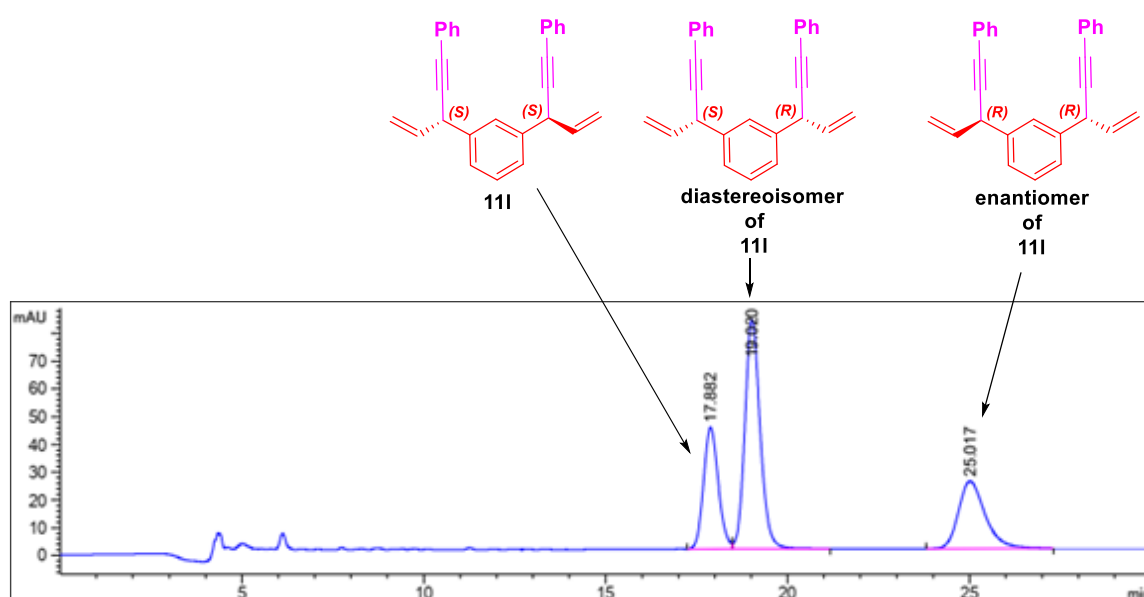
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.779	BV	0.1363	1576.14478	179.79816	50.1491
2	9.340	VB	0.1448	1566.77307	168.01320	49.8509
Totals :				3142.91785	347.81136	

SUPPORTING INFORMATION

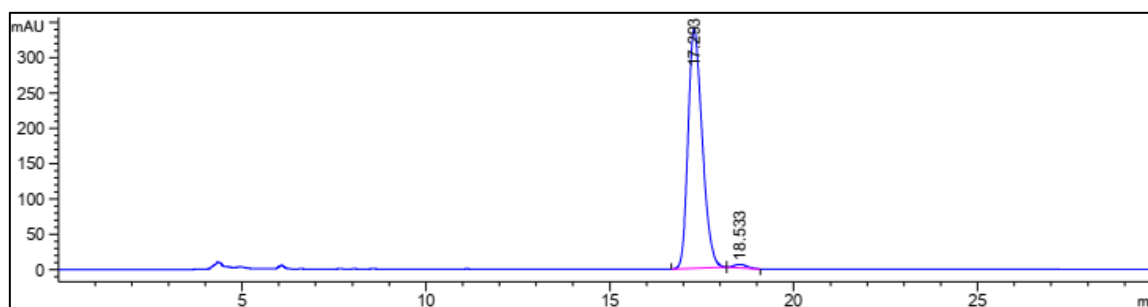
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.882	BV	0.4371	1235.99634	43.81936	25.2751
2	19.020	VB	0.4497	2415.48242	82.48162	49.3946
3	25.017	BB	0.7499	1238.69666	24.25213	25.3303

Totals : 4890.17542 150.55311

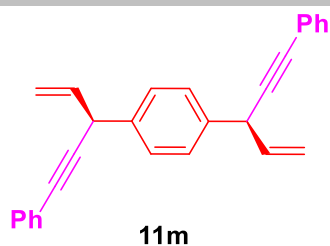
(*S,S*)- Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.293	BB	0.4149	9094.74219	339.15292	98.6857
2	18.533	BB	0.3738	121.12226	5.08692	1.3143

Totals : 9215.86445 344.23984

SUPPORTING INFORMATION



Colorless oil. 80.0 mg, 56% yield. $[\alpha]_D^{29}$: -116.5 ($c = 2.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, $\text{Chloroform-}d$) δ 7.54 – 7.47 (m, 2H), 7.45 (s, 2H), 7.38 – 7.30 (m, 3H), 6.03 (ddd, $J = 16.7, 9.9, 6.1$ Hz, 1H), 5.49 (d, $J = 16.9$ Hz, 1H), 5.22 (d, $J = 9.9$ Hz, 1H), 4.61 (d, $J = 6.1$ Hz, 1H).

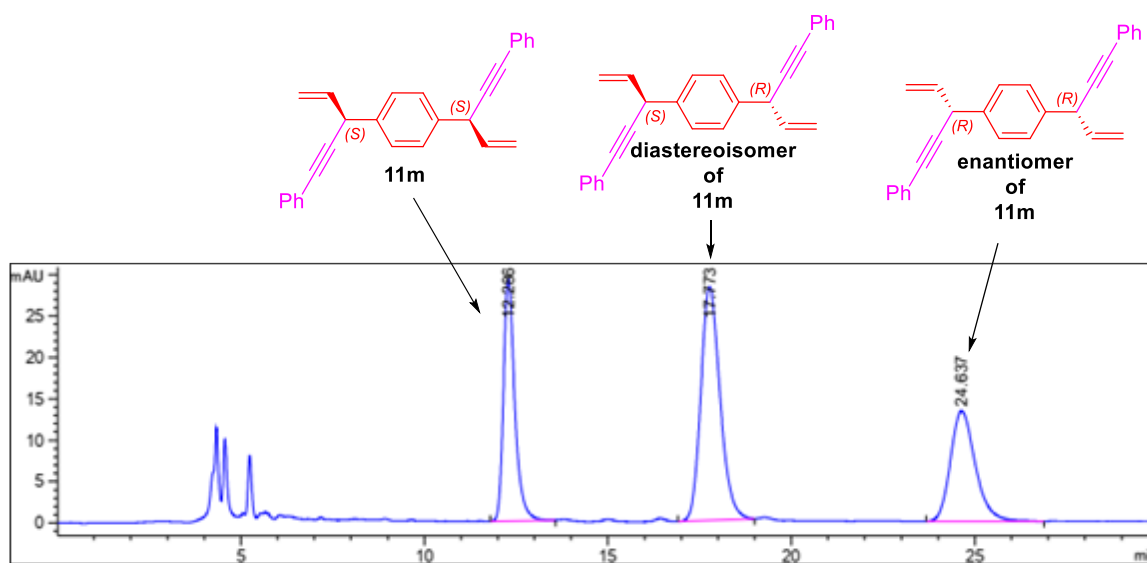
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.97, 137.83, 131.68, 128.23, 127.99, 127.98, 123.47, 115.31, 88.62, 85.33, 41.63.

HRMS (APCI): $[\text{M}]^+$ Calcd. for $[\text{C}_{28}\text{H}_{22}]^+$ 358.1717, found 358.1722.

IR (neat): 3080, 3055, 3018, 2928, 2856, 2199, 1636, 1599, 1508, 1491, 1443, 1215, 988, 916, 752, 690 cm^{-1} .

HPLC: Daicel Chiralcel[®] OJ-H, 10% i PrOH, 90% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee*, 31:1 *dr* (t_{R} (major) = 12.06 min, t_{R} (minor) = 17.62 min [peak of diastereoisomer]).

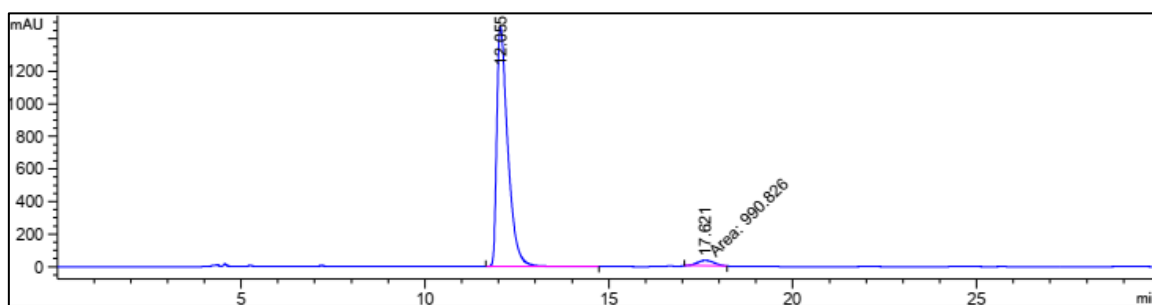
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.286	BB	0.3241	626.07587	29.20801	27.4015
2	17.773	BB	0.5563	1027.26184	28.24463	44.9602
3	24.637	BB	0.7039	631.48944	13.34980	27.6384
Totals :				2284.82715	70.80243	

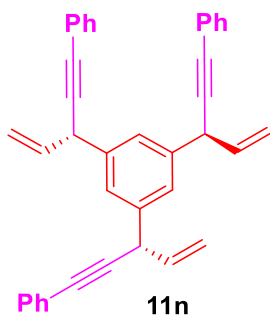
SUPPORTING INFORMATION

(*S,S*)- Enantioenriched



Peak Table

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.055	BB	0.3108	3.05596e4	1468.50818	96.8595
2	17.621	MM	0.5101	990.82617	32.37307	3.1405
Totals :				3.15504e4	1500.88125	



Colorless oil. 109.6 mg, 55% yield. $[\alpha]_D^{29}$: -82.40 ($c = 2.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 – 7.37 (m, 3H), 7.32 – 7.19 (m, 3H), 6.02 (ddd, $J = 16.3, 9.8, 6.3$ Hz, 1H), 5.47 (dt, $J = 16.9, 1.5$ Hz, 1H), 5.21 (dt, $J = 9.8, 1.5$ Hz, 1H), 4.61 (d, $J = 6.3$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.88, 137.73, 131.70, 128.22, 127.95, 125.83, 123.45, 115.57, 88.54, 85.52, 41.93.

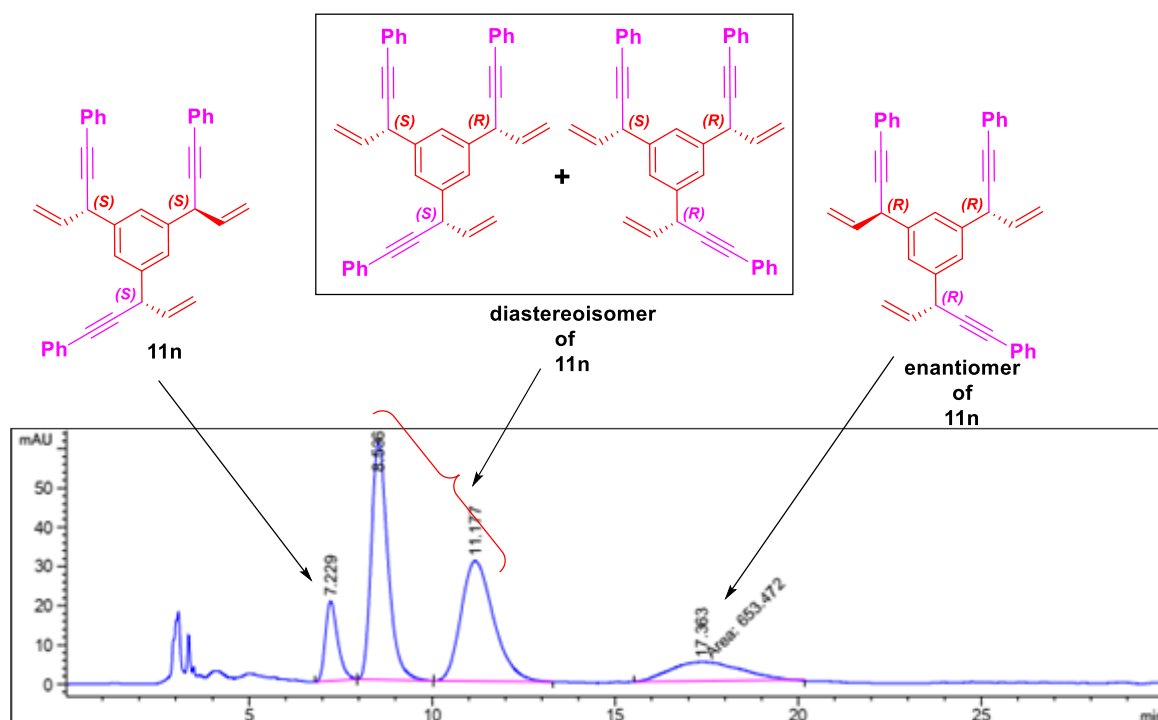
HRMS (APCI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{39}\text{H}_{31}]^+$ **499.2421**, found 499.2424.

IR (neat): 3082, 3057, 3018, 2926, 2201, 1639, 1599, 1491, 1445, 1215, 1070, 989, 926, 750, 690 cm^{-1} .

HPLC: Daicel Chiralcel® OJ-H, 20% *i*PrOH, 80% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee*, 43:1 *dr* (t_R (major) = 7.23 min, t_R (minor) = 8.56 min [peak of diastereoisomer]).

SUPPORTING INFORMATION

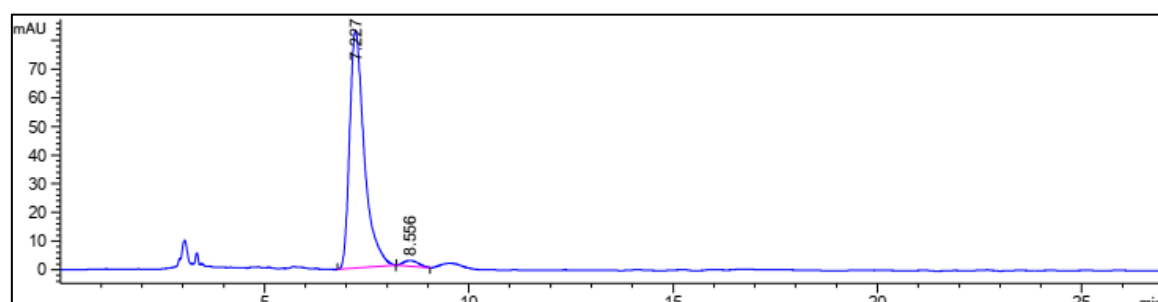
Racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.229	BB	0.3587	474.38565	20.29615	9.6029
2	8.536	BB	0.4847	1912.61560	60.52533	38.7167
3	11.177	BB	0.9349	1899.55432	30.65520	38.4523
4	17.363	MM	2.2509	653.47205	4.83870	13.2281

Totals : 4940.02762 116.31538

(S,S,S)- Enantioenriched



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.227	BB	0.3753	2066.32422	82.76975	97.7213
2	8.556	BB	0.3508	48.18363	1.93334	2.2787

Totals : 2114.50785 84.70310

SUPPORTING INFORMATION

Crystallographic Data

1) X-ray diffraction of (S,R)-4 (CCDC 2126362)

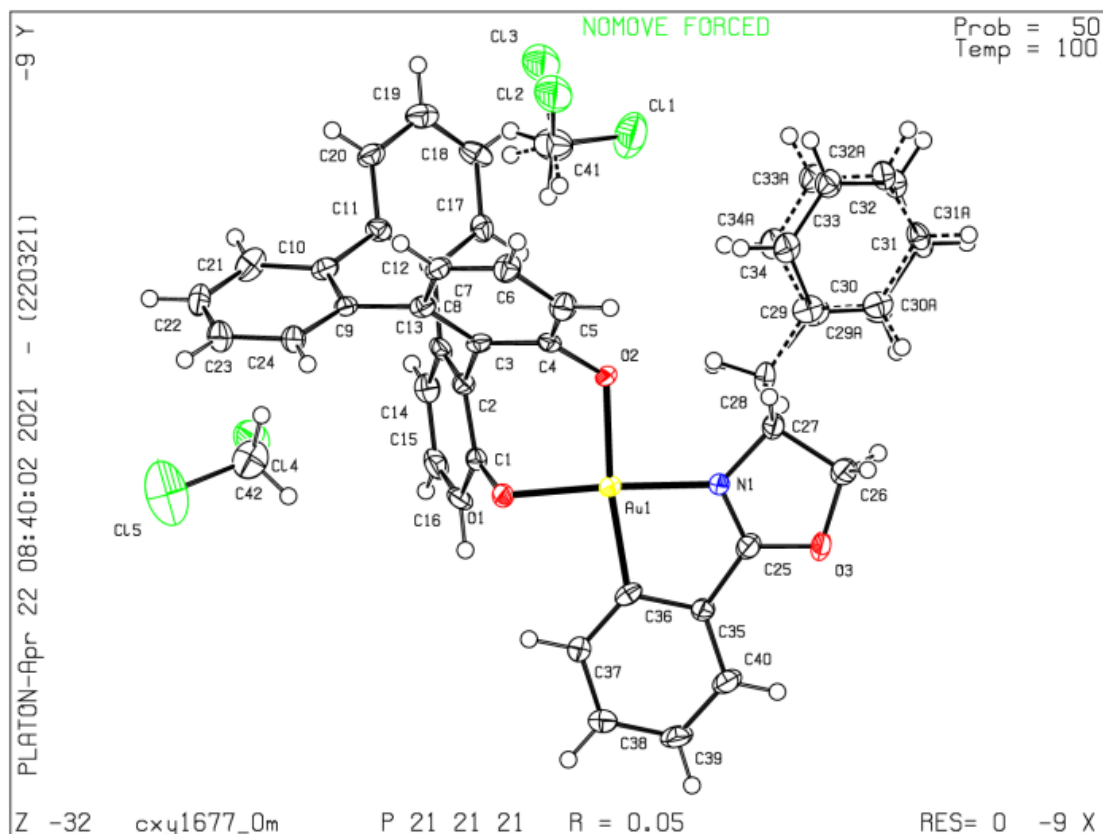


Table S2 Crystal data and structure refinement for (S,R)-4.

Identification code	cxy1677_0m
Empirical formula	C ₄₂ H ₃₂ AuCl ₄ NO ₃
Formula weight	937.45
Temperature/K	100
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	12.5780(10)
b/Å	13.7123(11)
c/Å	21.0398(15)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3628.8(5)
Z	4
ρ _{calc} /cm ³	1.716
μ/mm ⁻¹	4.391
F(000)	1848.0
Crystal size/mm ³	0.35 × 0.32 × 0.28

SUPPORTING INFORMATION

Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^{\circ}$	4.394 to 56.886
Index ranges	$-16 \leq h \leq 16$, $-18 \leq k \leq 18$, $-28 \leq l \leq 25$
Reflections collected	70184
Independent reflections	9114 [$R_{\text{int}} = 0.0524$, $R_{\text{sigma}} = 0.0284$]
Data/restraints/parameters	9114/243/482
Goodness-of-fit on F^2	1.144
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0493$, $wR_2 = 0.1205$
Final R indexes [all data]	$R_1 = 0.0506$, $wR_2 = 0.1212$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	5.10/-4.56
Flack parameter	0.024(3)

2) X-ray diffraction of (*R,S*)-4 (CCDC 2126367)

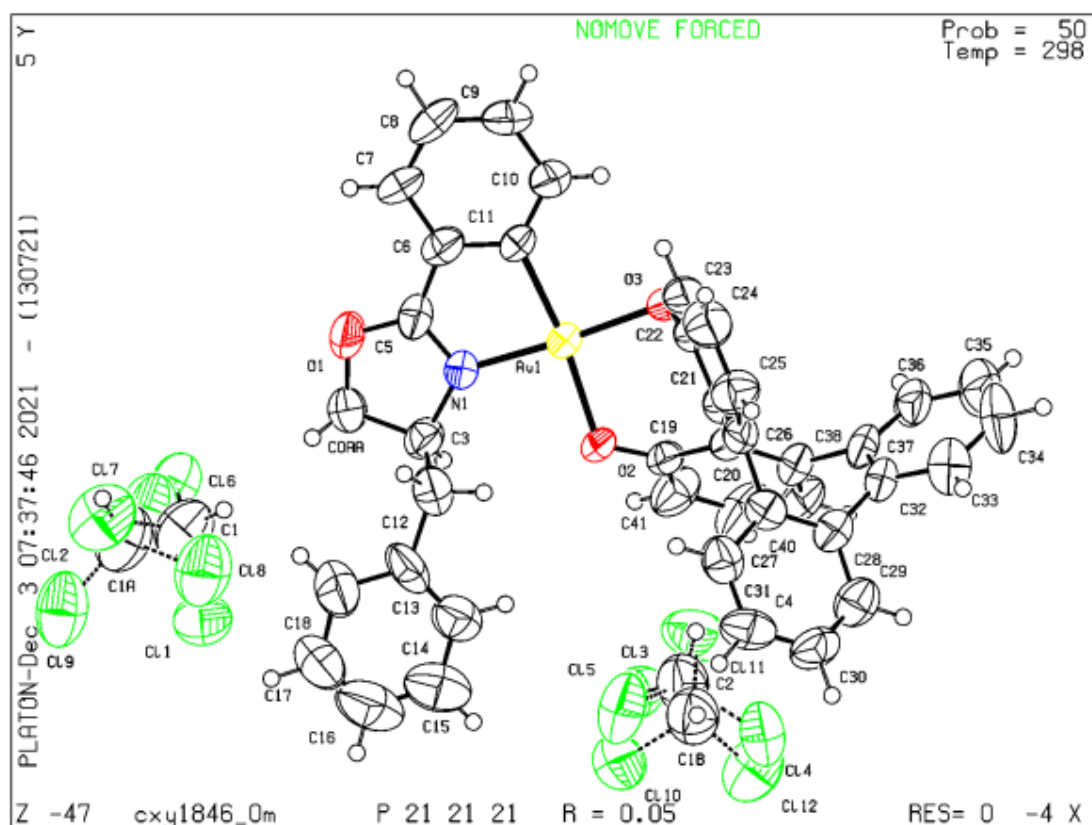


Table S3 Crystal data and structure refinement for (*R,S*)-4.

Identification code	cxy1846_0m
Empirical formula	$C_{41.17}H_{29.17}AuCl_{3.5}NO_3$
Formula weight	906.87
Temperature/K	298
Crystal system	orthorhombic
Space group	$P2_12_12_1$

SUPPORTING INFORMATION

a/Å	12.999(5)
b/Å	13.954(4)
c/Å	22.150(8)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	4018(2)
Z	4
ρ_{calc} /cm ³	1.499
μ /mm ⁻¹	3.931
F(000)	1783.0
Crystal size/mm ³	0.31 × 0.24 × 0.22
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.66 to 54.672
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 15, -25 ≤ l ≤ 28
Reflections collected	37984
Independent reflections	9044 [R _{int} = 0.0454, R _{sigma} = 0.0479]
Data/restraints/parameters	9044/270/550
Goodness-of-fit on F ²	1.071
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0476, wR ₂ = 0.1201
Final R indexes [all data]	R ₁ = 0.0723, wR ₂ = 0.1338
Largest diff. peak/hole / e Å ⁻³	1.20/-0.98
Flack parameter	-0.013(4)

SUPPORTING INFORMATION

3) X-ray diffraction of (*S,S*)-4 (CCDC 2126368)

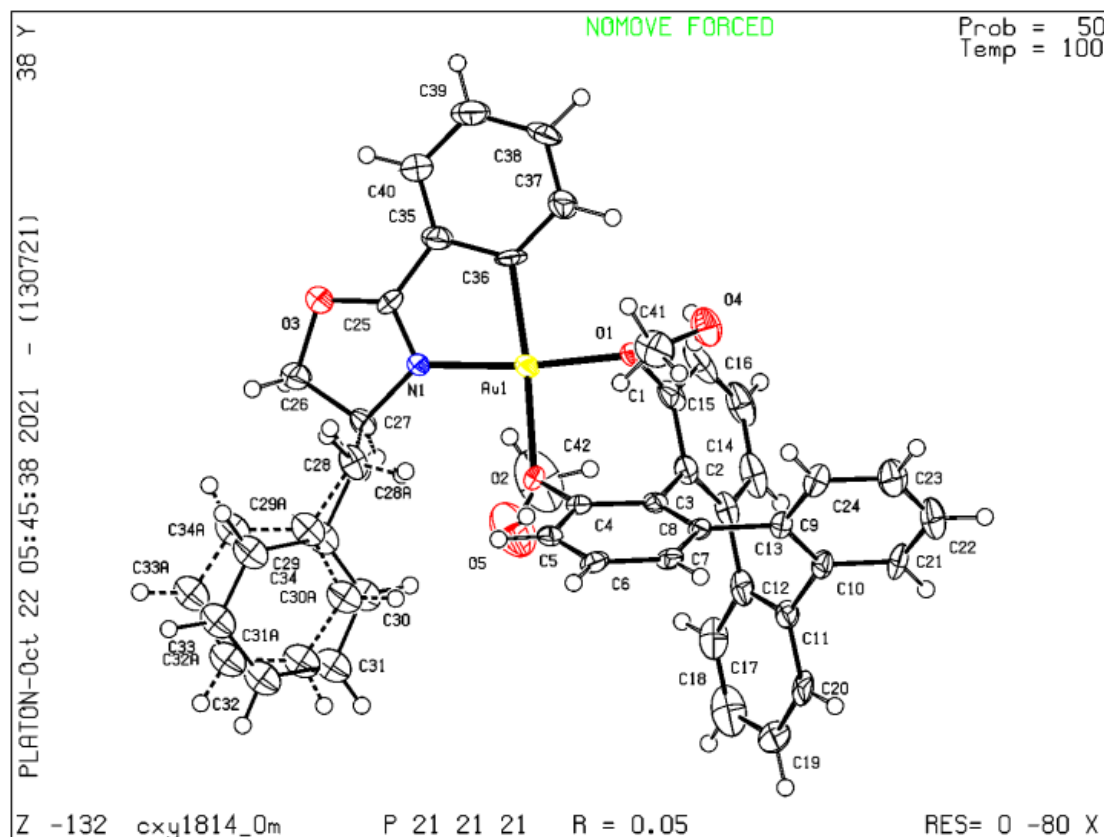


Table S4 Crystal data and structure refinement for (*S,S*)-4.

Identification code	cxy1814_0m
Empirical formula	C ₄₂ H ₃₆ AuNO ₅
Formula weight	831.68
Temperature/K	100
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.9266(7)
b/Å	13.1669(9)
c/Å	27.3976(19)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3580.9(4)
Z	4
ρ _{calc} /cm ³	1.543
μ/mm ⁻¹	4.154
F(000)	1656.0
Crystal size/mm ³	0.32 × 0.31 × 0.25
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.068 to 55.106
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -35 ≤ l ≤ 35

SUPPORTING INFORMATION

Reflections collected	84689
Independent reflections	8230 [$R_{\text{int}} = 0.0994$, $R_{\text{sigma}} = 0.0491$]
Data/restraints/parameters	8230/221/469
Goodness-of-fit on F^2	1.260
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0512$, $wR_2 = 0.1213$
Final R indexes [all data]	$R_1 = 0.0595$, $wR_2 = 0.1231$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	2.53/-3.12
Flack parameter	0.007(4)

4) X-ray diffraction of (*R,R*)-4 (CCDC 2126366)

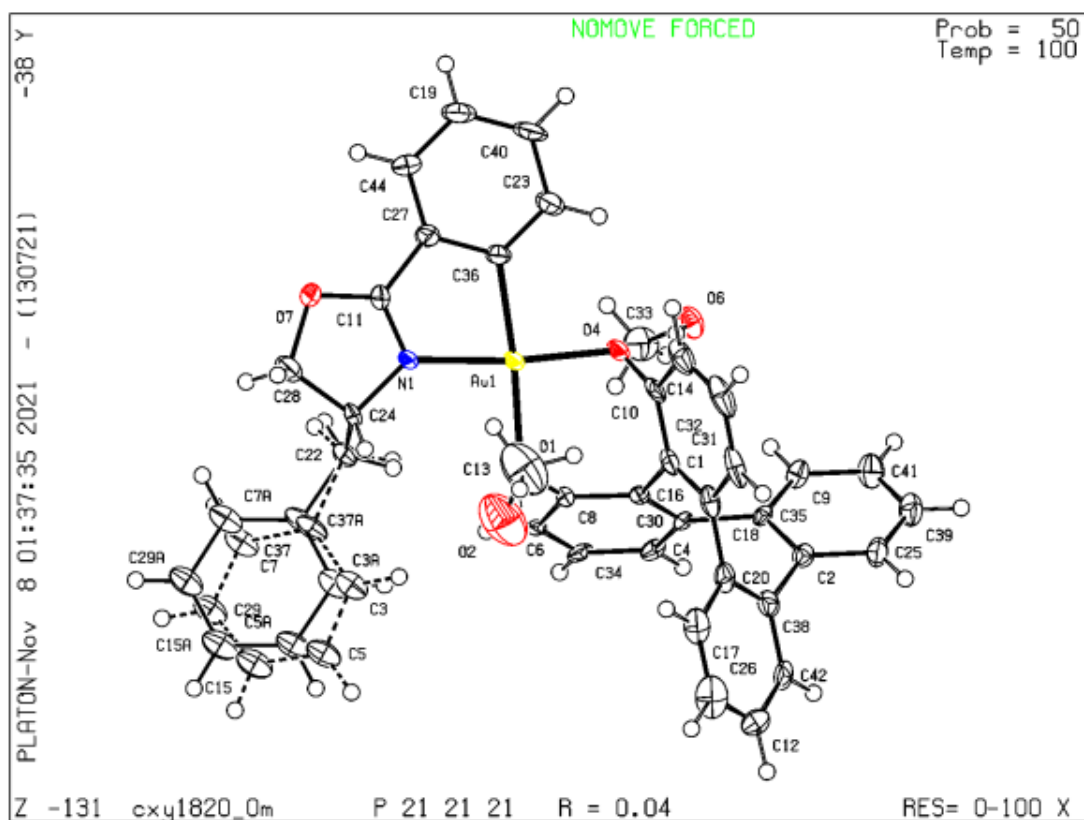


Table S5 Crystal data and structure refinement for (*R,R*)-4.

Identification code	cxy1820_0m
Empirical formula	$\text{AuC}_{43}\text{H}_{40}\text{NO}_6$
Formula weight	863.72
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
$a/\text{\AA}$	9.9306(6)
$b/\text{\AA}$	13.2468(9)
$c/\text{\AA}$	27.4297(18)

SUPPORTING INFORMATION

$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3608.3(4)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.590
μ/mm^{-1}	4.128
F(000)	1728.0
Crystal size/ mm^3	$0.31 \times 0.24 \times 0.19$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.274 to 56.712
Index ranges	$-13 \leq h \leq 13, -17 \leq k \leq 17, -36 \leq l \leq 36$
Reflections collected	53502
Independent reflections	8989 [$R_{\text{int}} = 0.0615, R_{\text{sigma}} = 0.0427$]
Data/restraints/parameters	8989/192/465
Goodness-of-fit on F^2	1.164
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0409, wR_2 = 0.0792$
Final R indexes [all data]	$R_1 = 0.0455, wR_2 = 0.0804$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.62/-3.40
Flack parameter	0.027(11)

SUPPORTING INFORMATION

5) X-ray diffraction of (S)-L1 (CCDC 2124171)

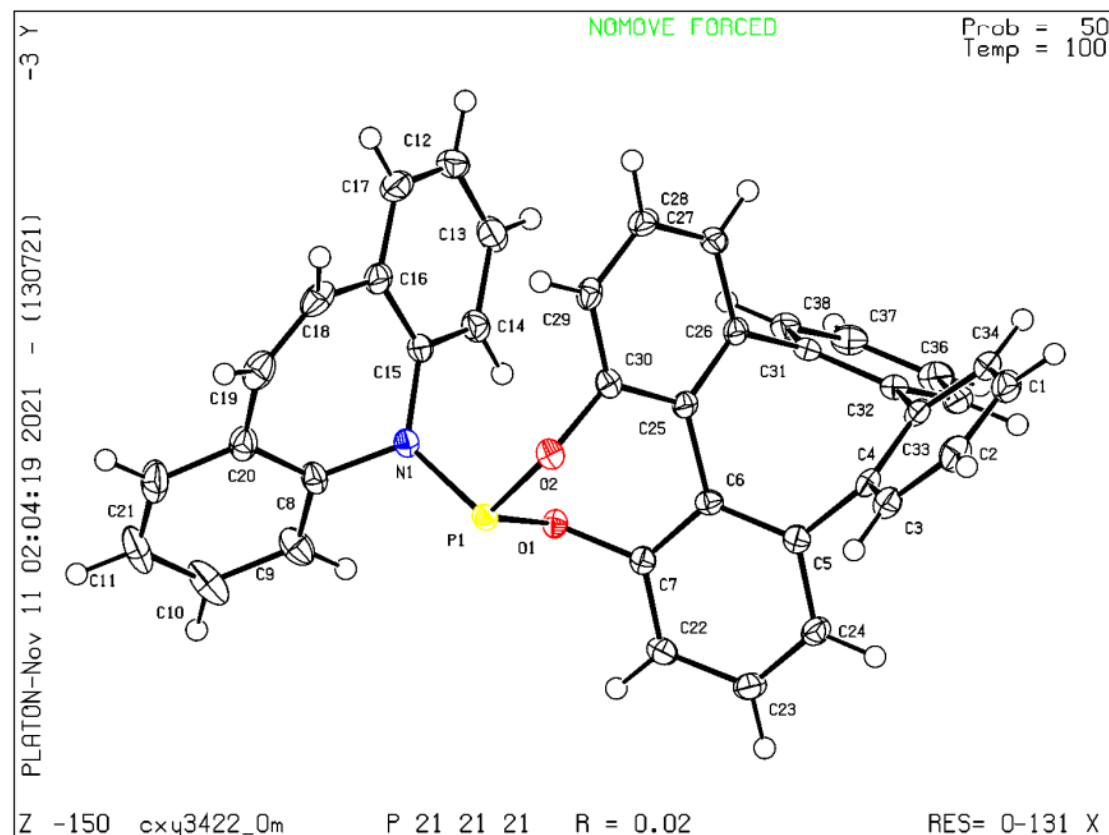


Table S6 Crystal data and structure refinement for (S)-L1.

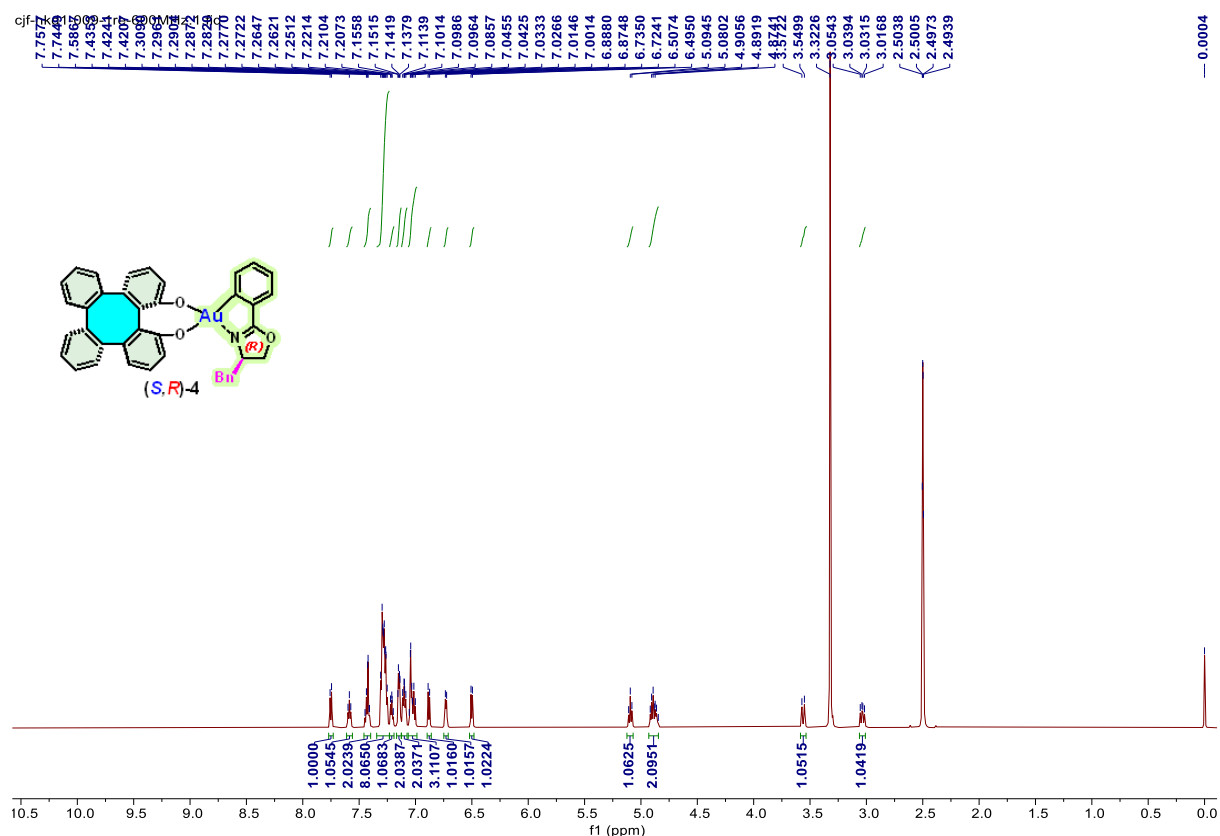
Identification code	cxy3422_0m
Empirical formula	C ₃₈ H ₂₄ NO ₂ P
Formula weight	557.55
Temperature/K	100
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	11.8935(6)
b/Å	12.6595(6)
c/Å	18.8734(10)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2841.7(2)
Z	4
ρ _{calc} /cm ³	1.303
μ/mm ⁻¹	1.139
F(000)	1160.0
Crystal size/mm ³	0.35 × 0.31 × 0.26
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	8.41 to 144.7
Index ranges	-13 ≤ h ≤ 14, -15 ≤ k ≤ 15, -20 ≤ l ≤ 23

SUPPORTING INFORMATION

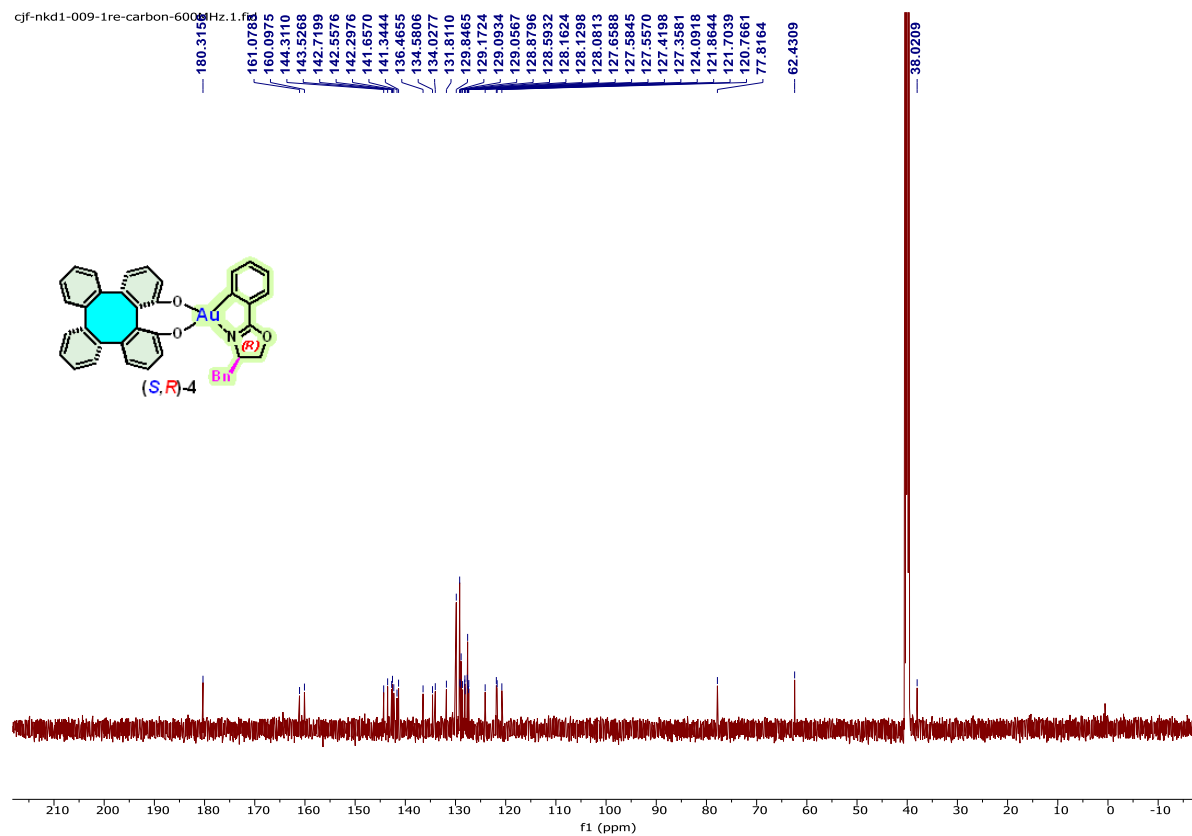
Reflections collected	34083
Independent reflections	5619 [$R_{\text{int}} = 0.0397$, $R_{\text{sigma}} = 0.0219$]
Data/restraints/parameters	5619/0/380
Goodness-of-fit on F^2	1.047
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0242$, $wR_2 = 0.0607$
Final R indexes [all data]	$R_1 = 0.0250$, $wR_2 = 0.0610$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.18/-0.21
Flack parameter	-0.002(4)

SUPPORTING INFORMATION

NMR spectra

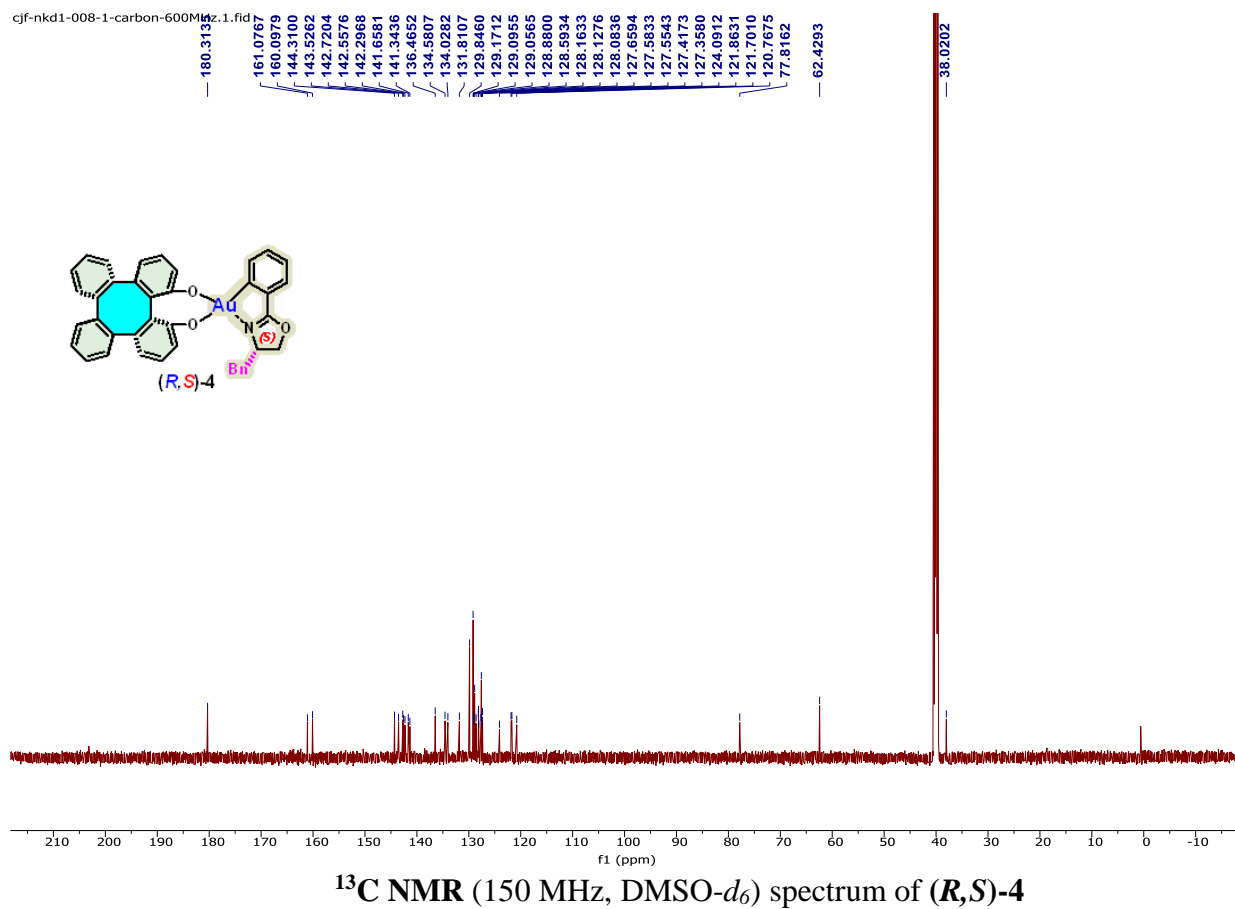
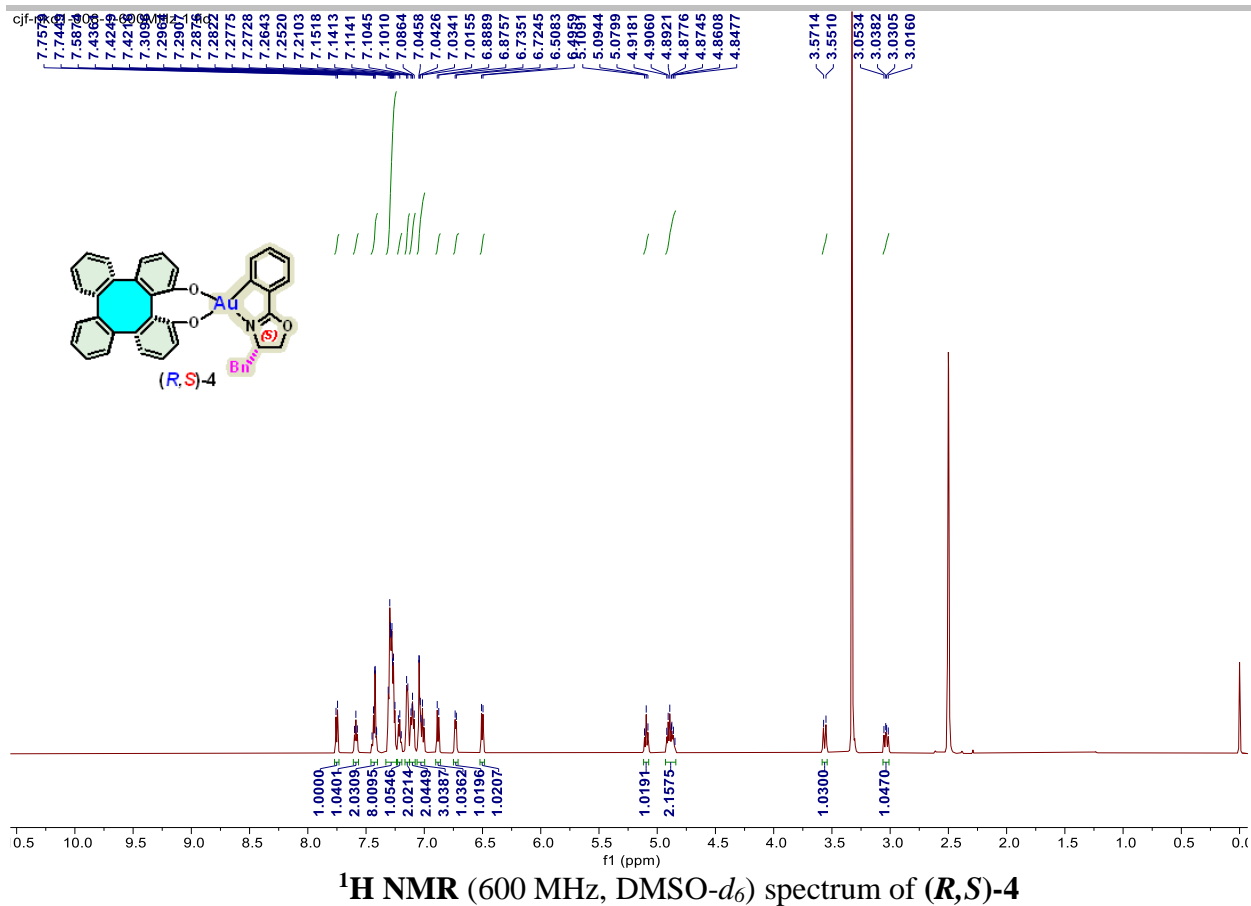


^1H NMR (600 MHz, $\text{DMSO-}d_6$) spectrum of (S,R) -4

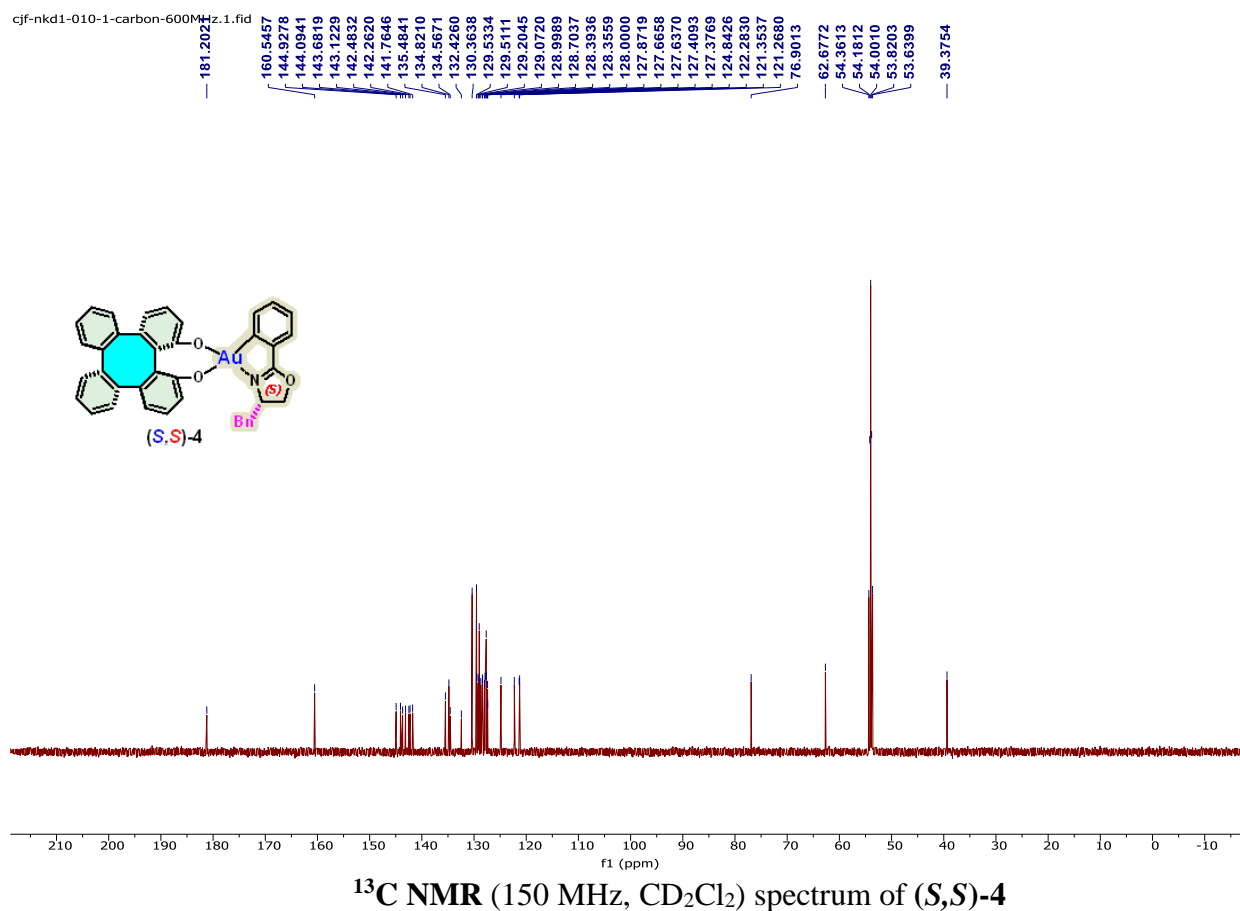
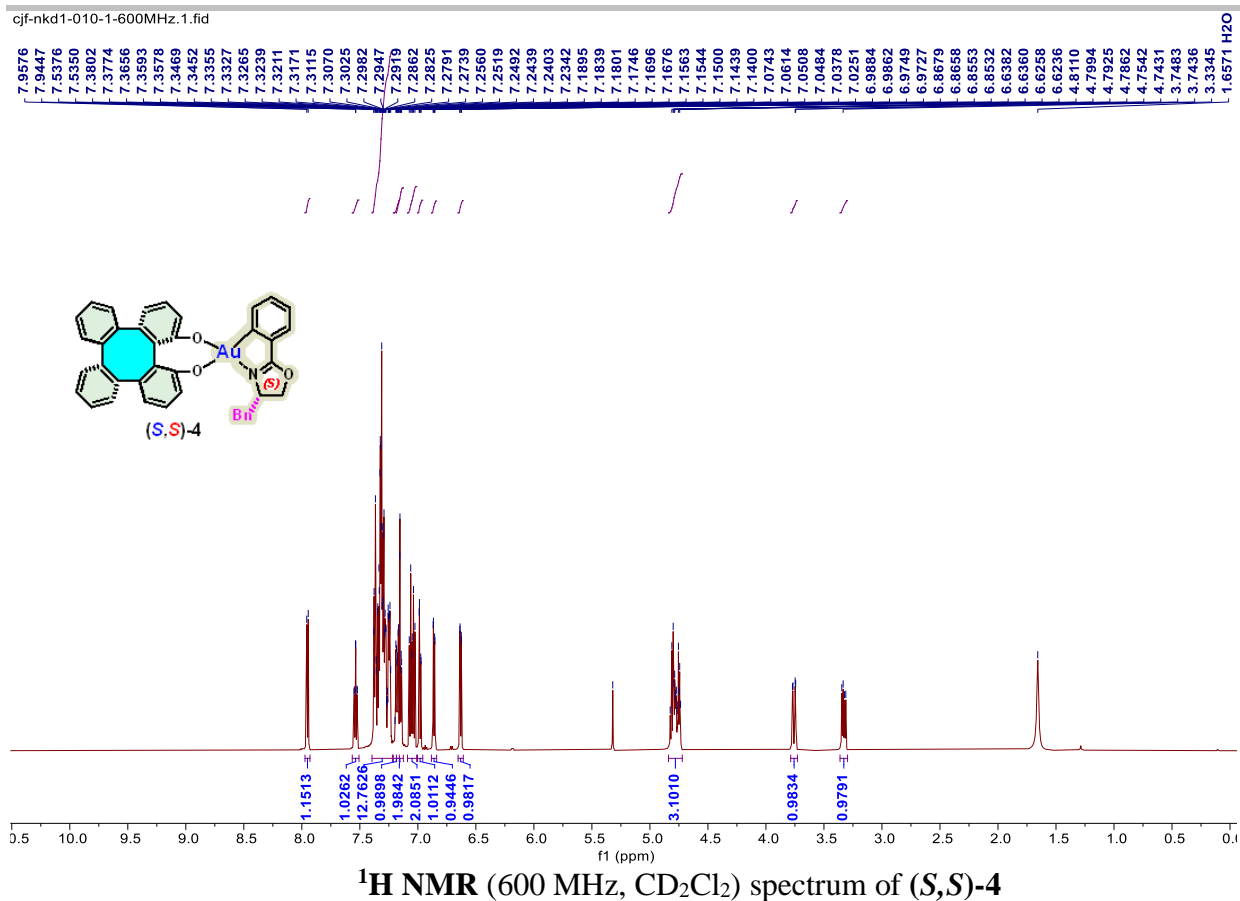


^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) spectrum of (S,R) -4

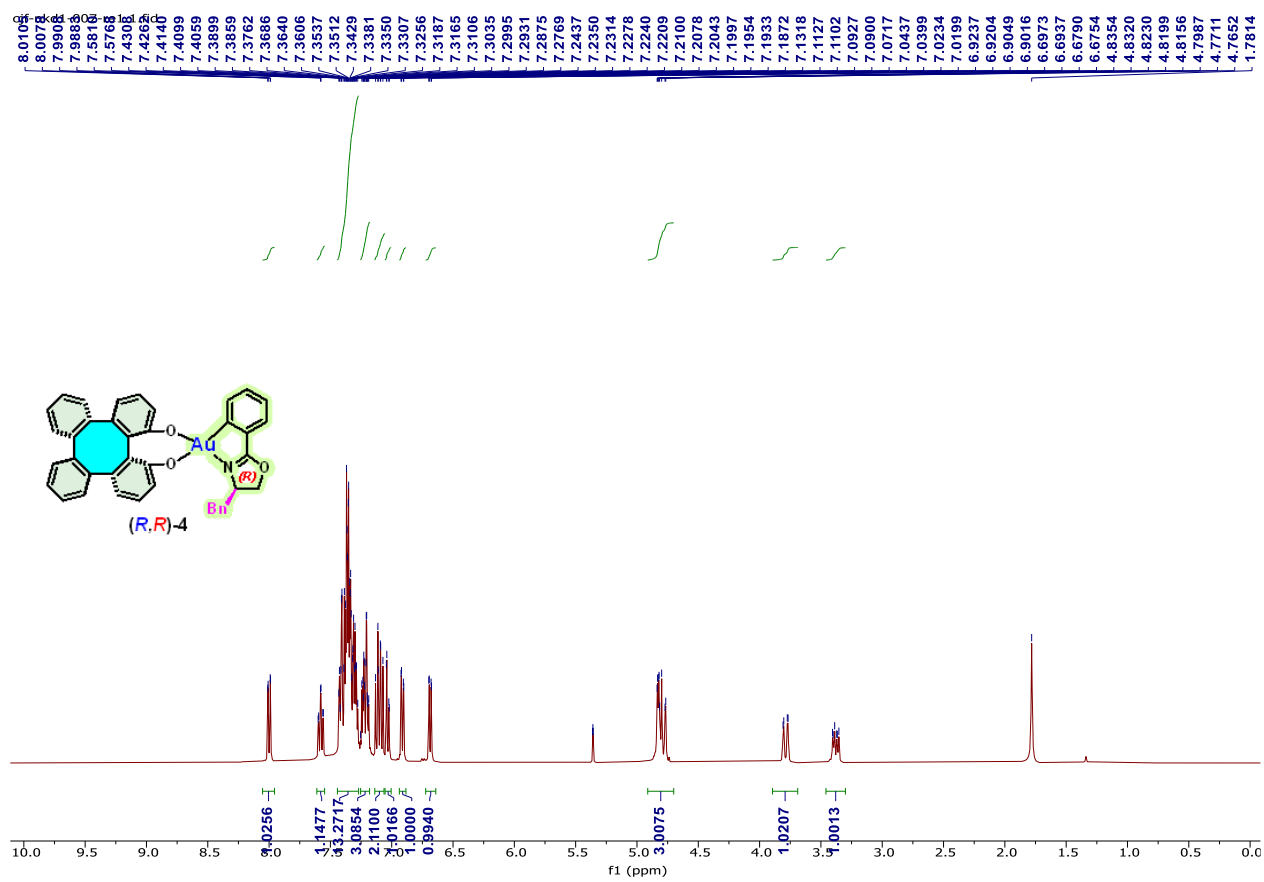
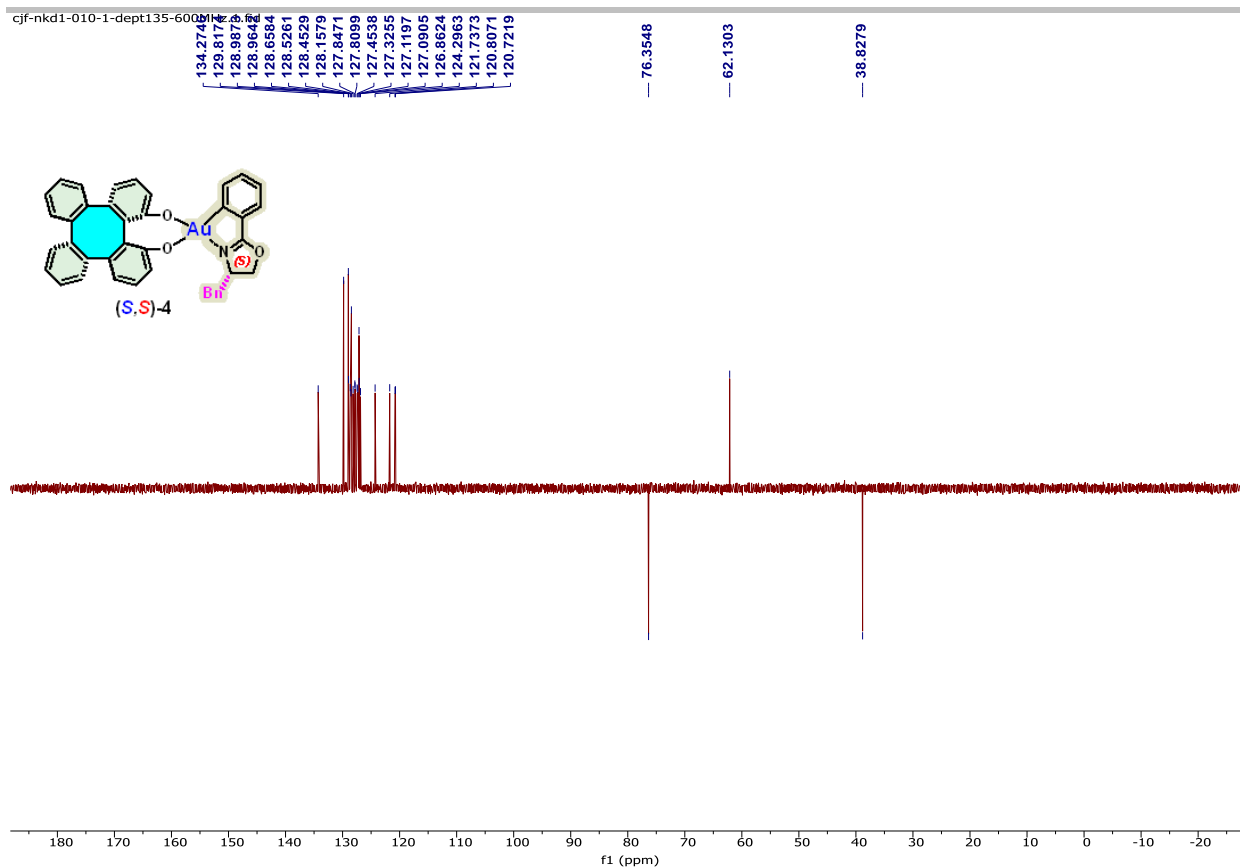
SUPPORTING INFORMATION



SUPPORTING INFORMATION

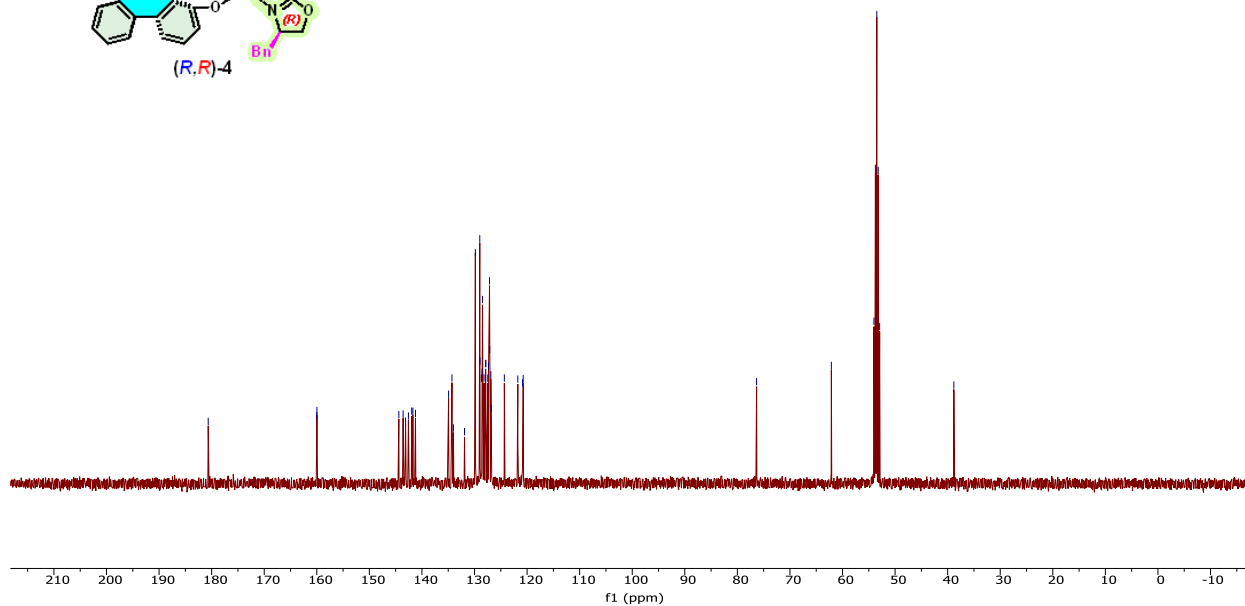
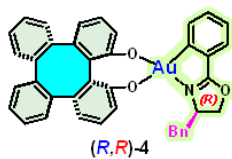


SUPPORTING INFORMATION



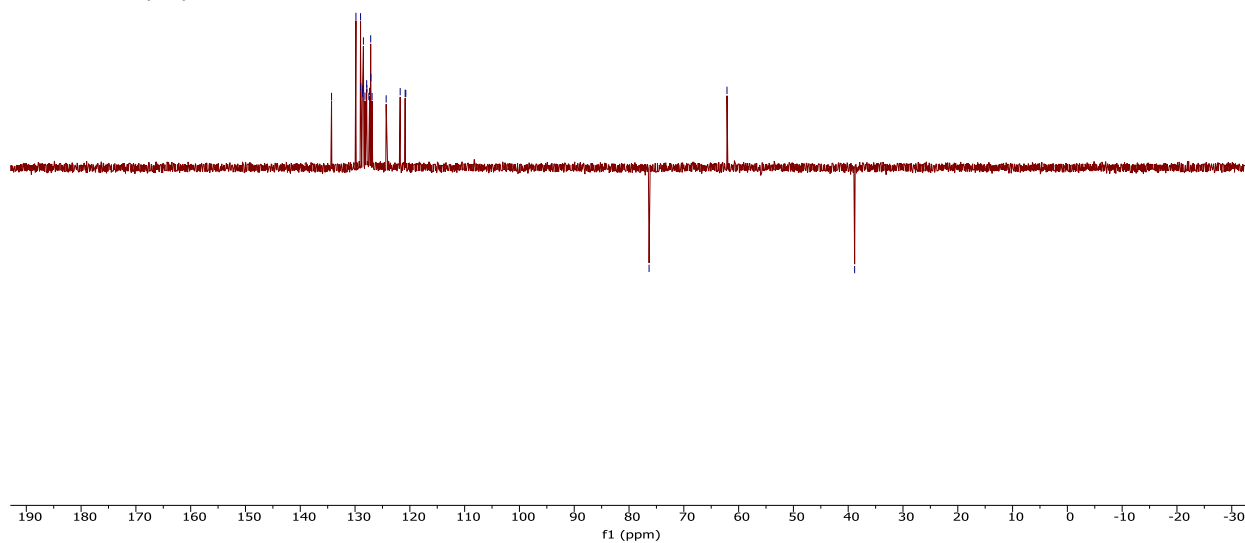
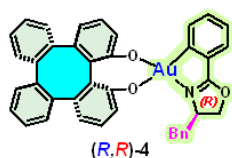
SUPPORTING INFORMATION

cfj-nkd1-007-re1-carbon.3.fid



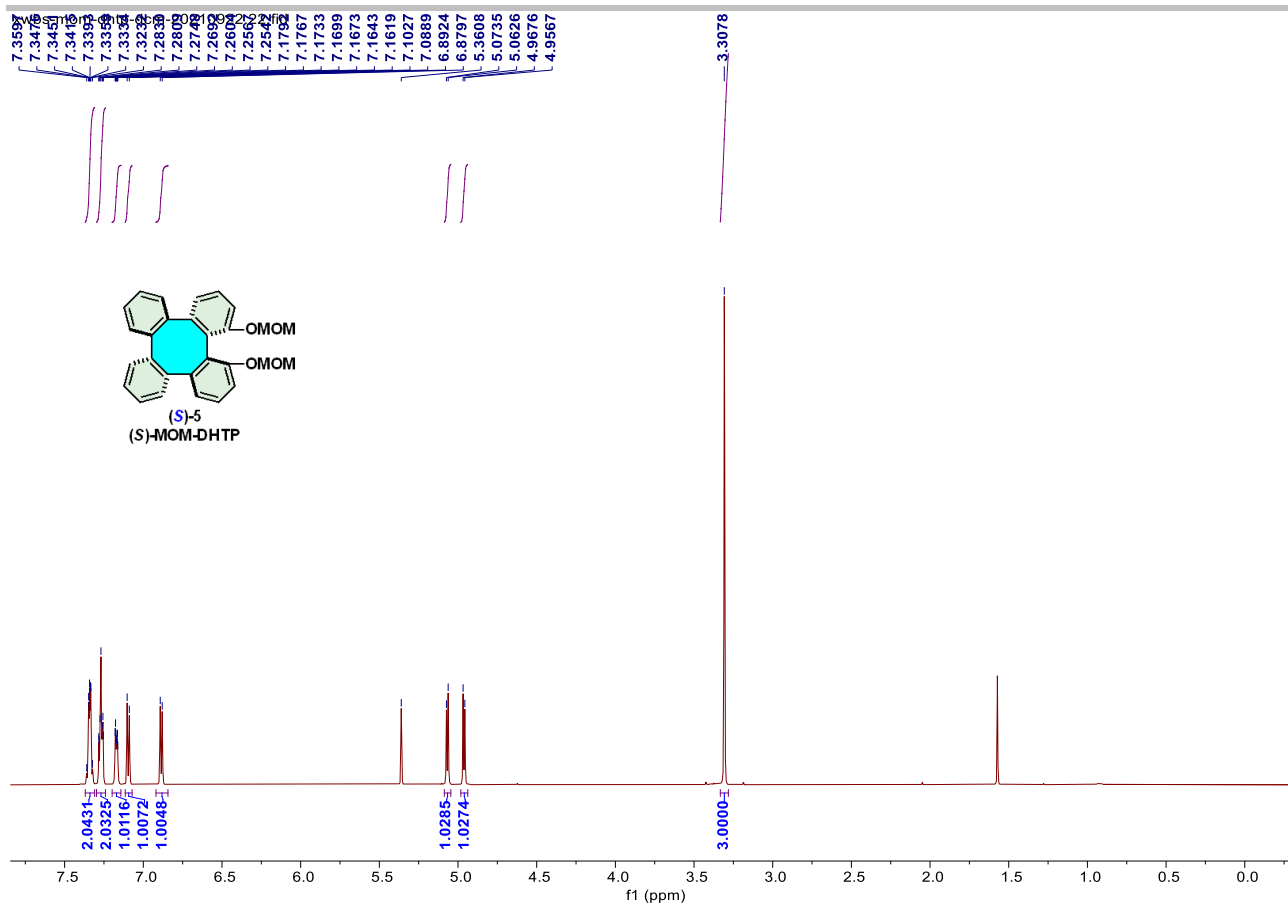
^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of **(R,R)-4**

cfj-nkd1-007-re1-dept135.2.fid

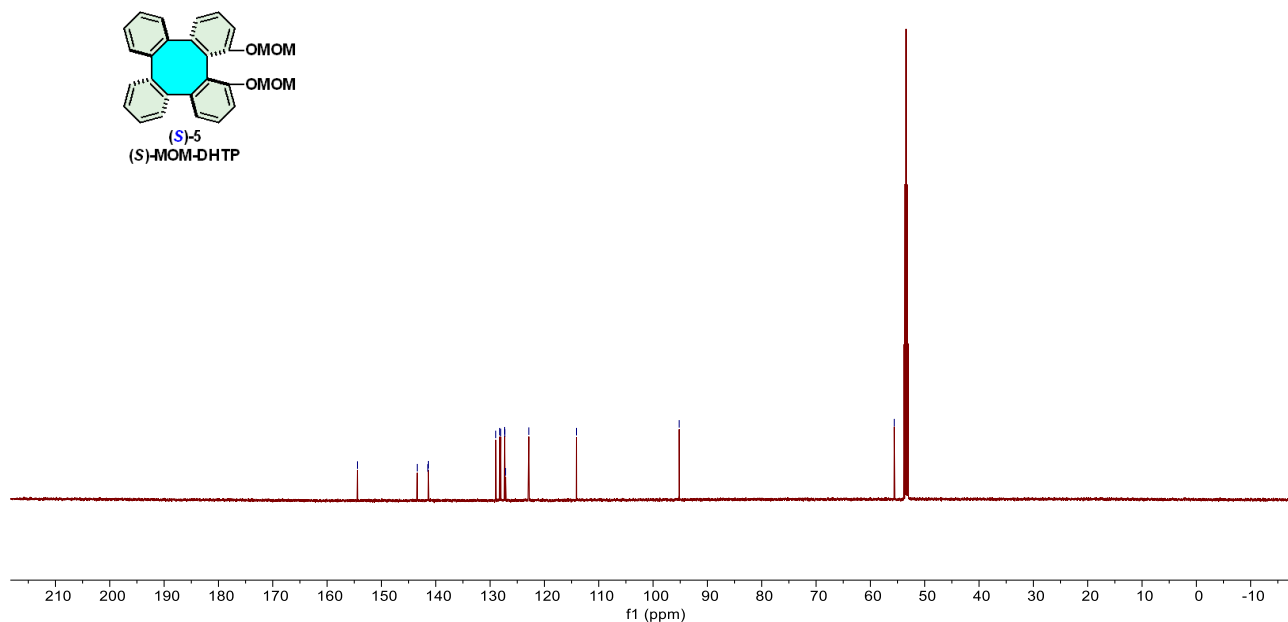


DEPT135 ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of **(R,R)-4**

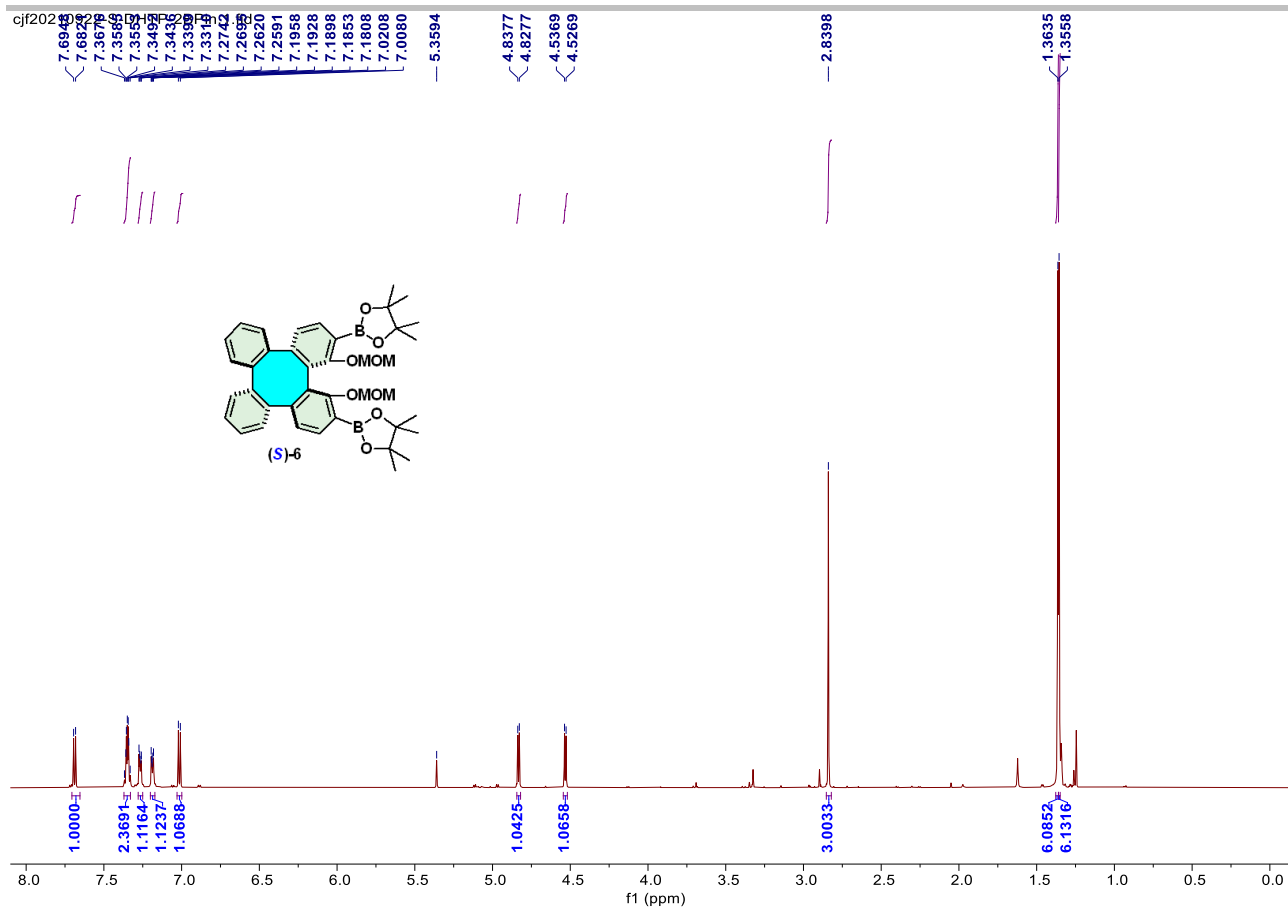
SUPPORTING INFORMATION



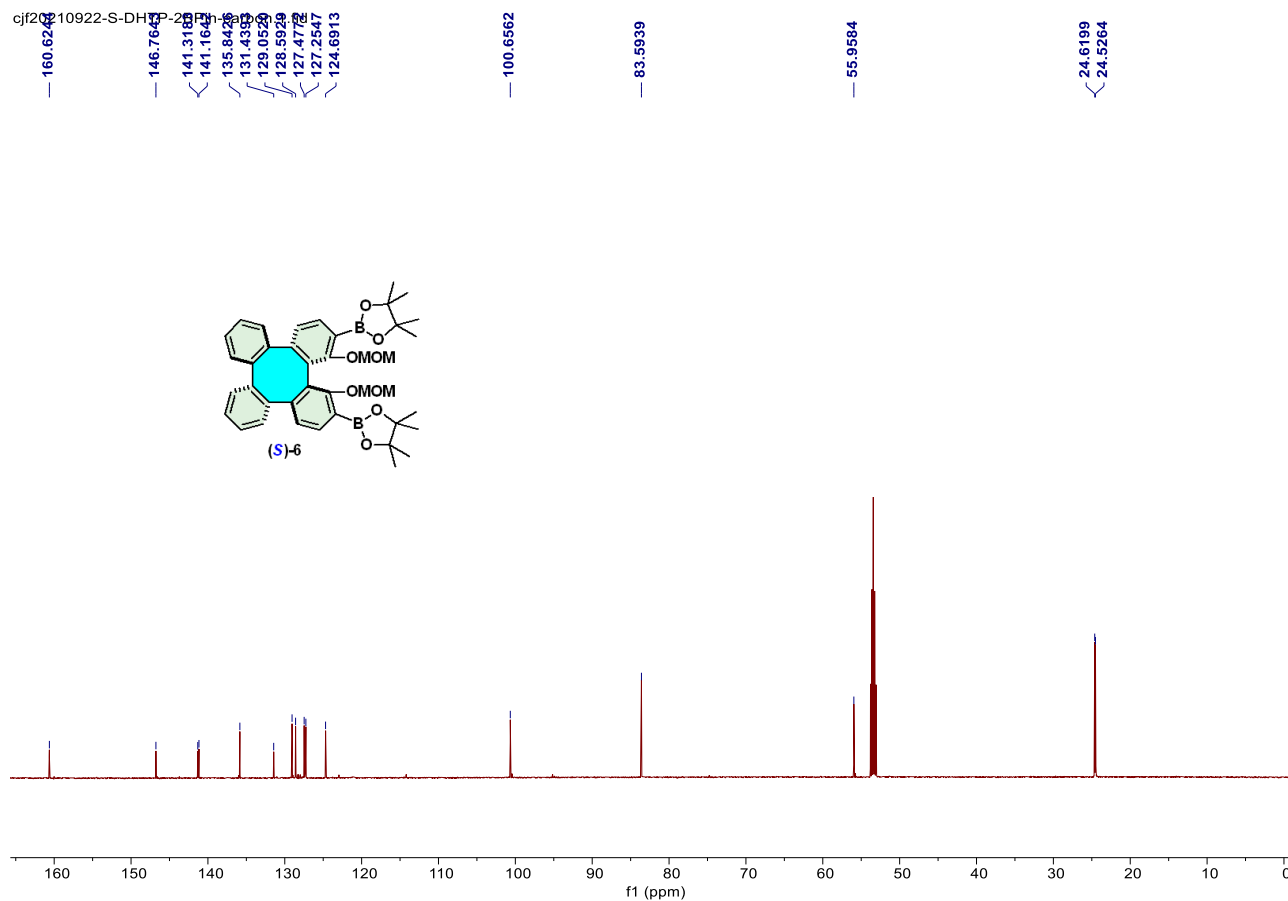
xwbs-mom-dhtp-dcm-20210922.23.fid



SUPPORTING INFORMATION

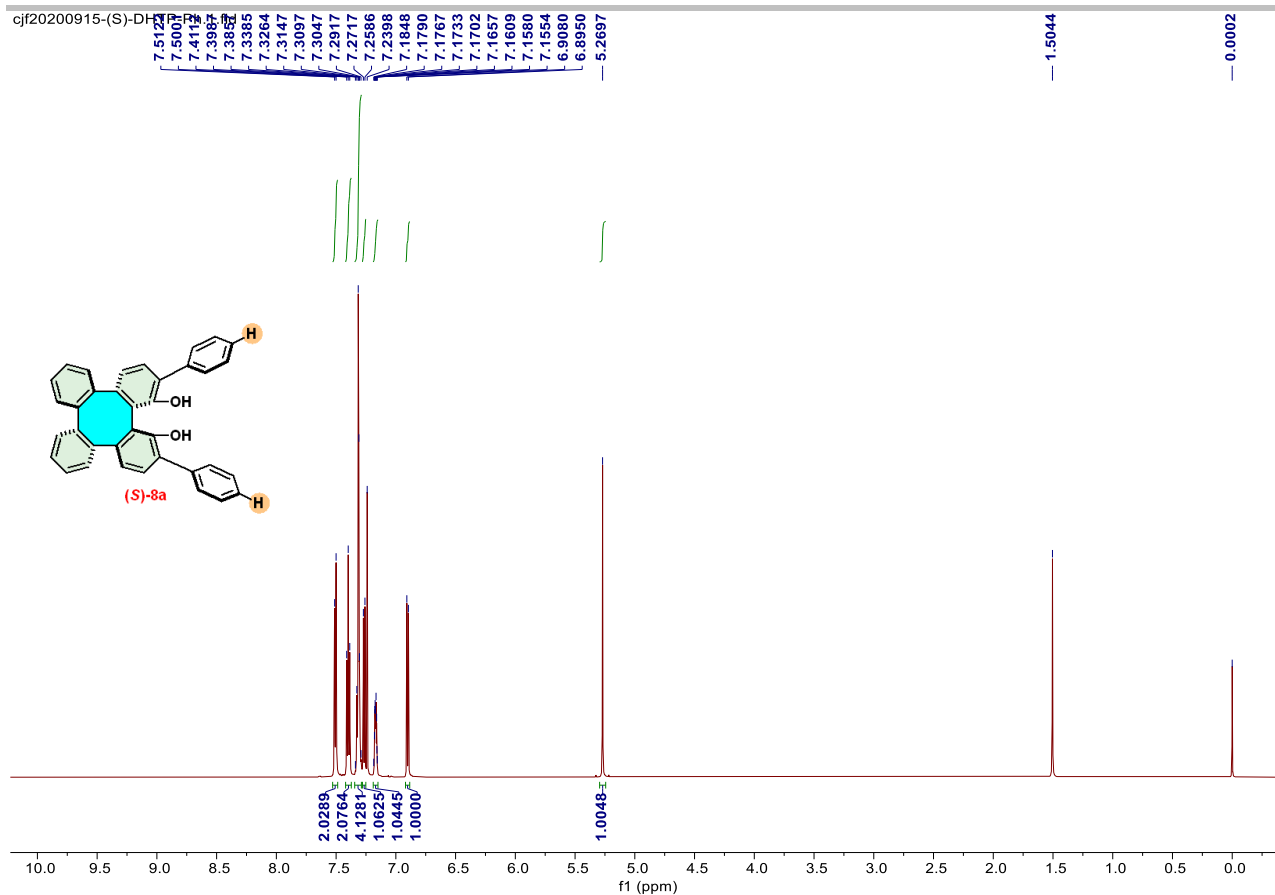


¹H NMR (600 MHz, CD₂Cl₂) spectrum of (S)-6

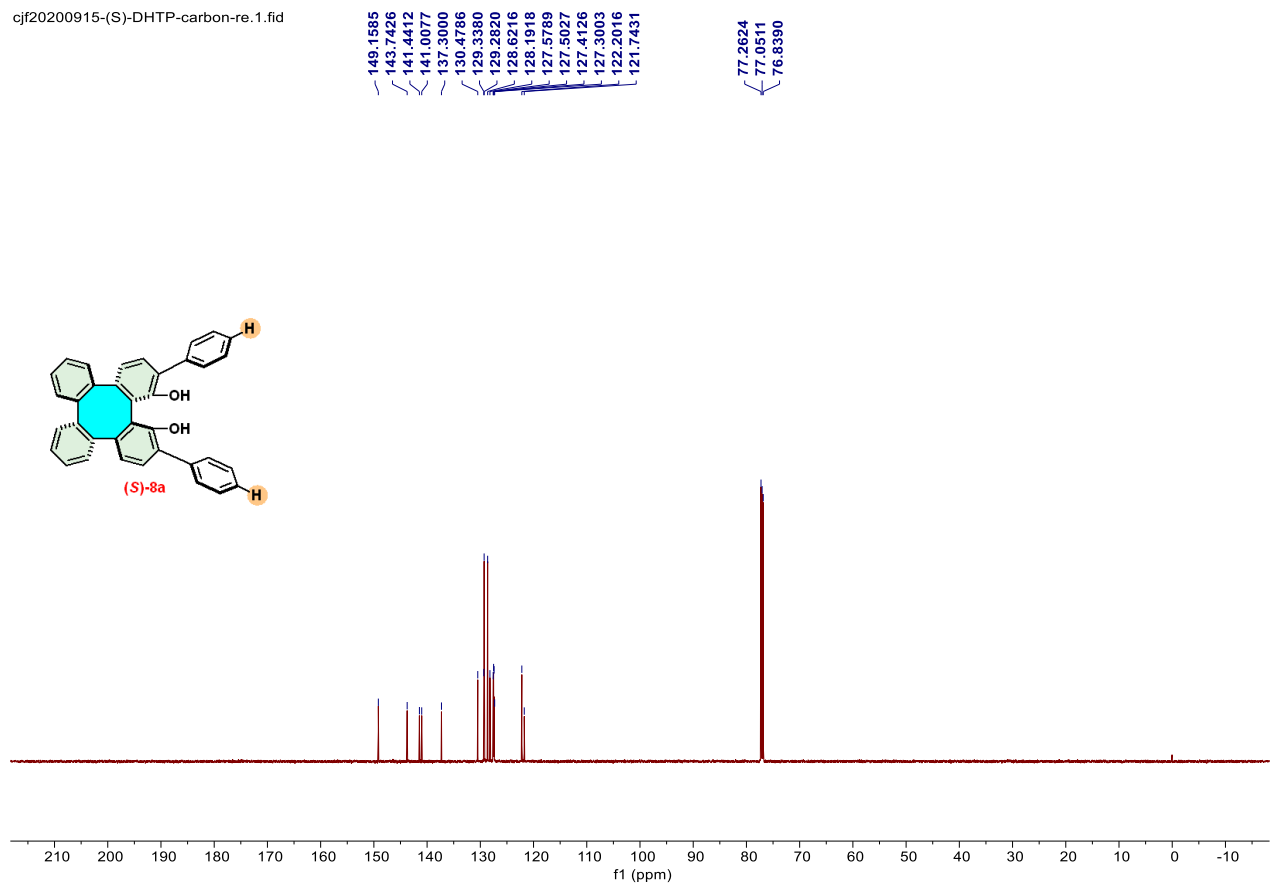


¹³C NMR (150 MHz, CD₂Cl₂) spectrum of (S)-6

SUPPORTING INFORMATION

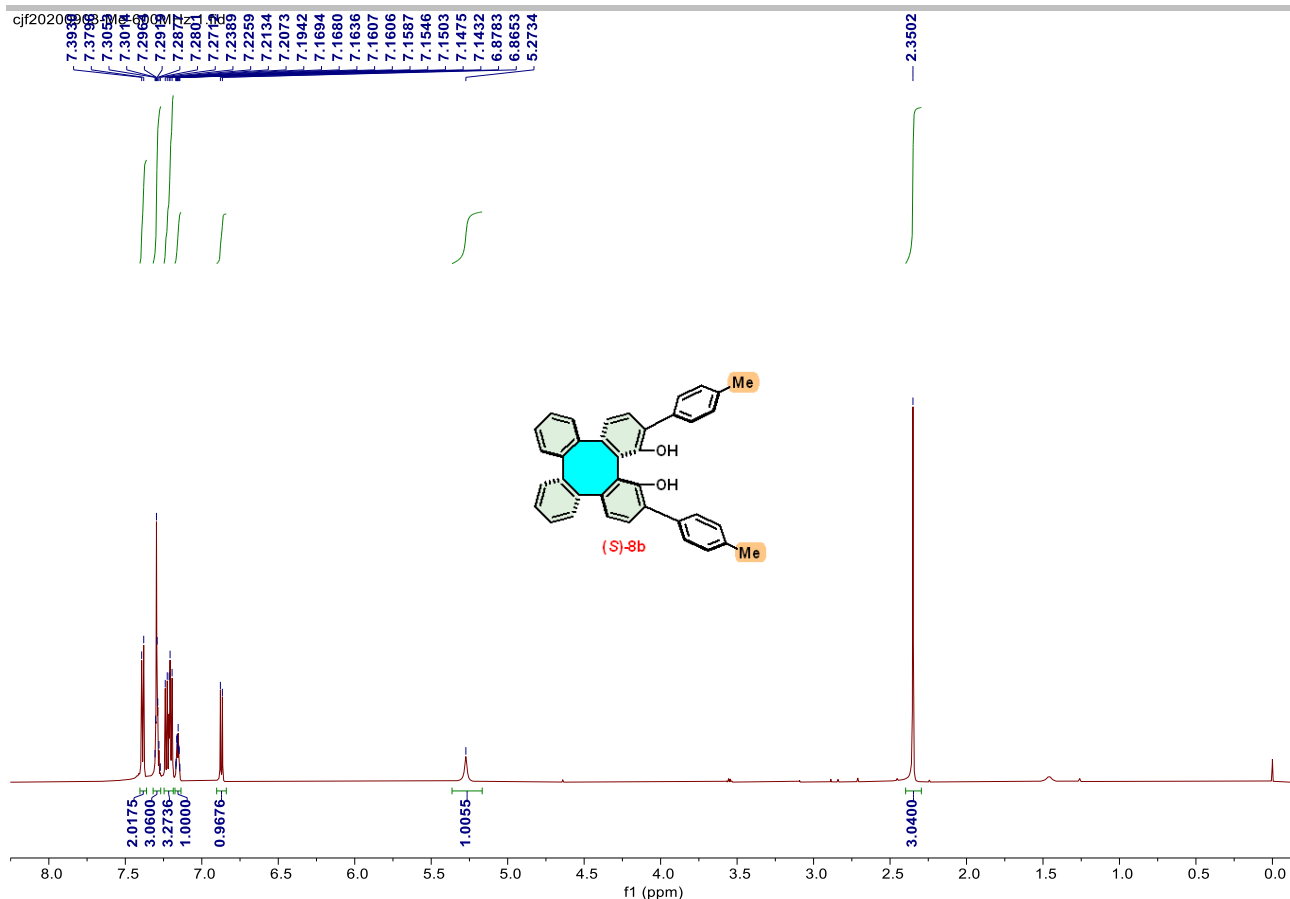


¹H NMR (600 MHz, CDCl₃) spectrum of (S)-8a

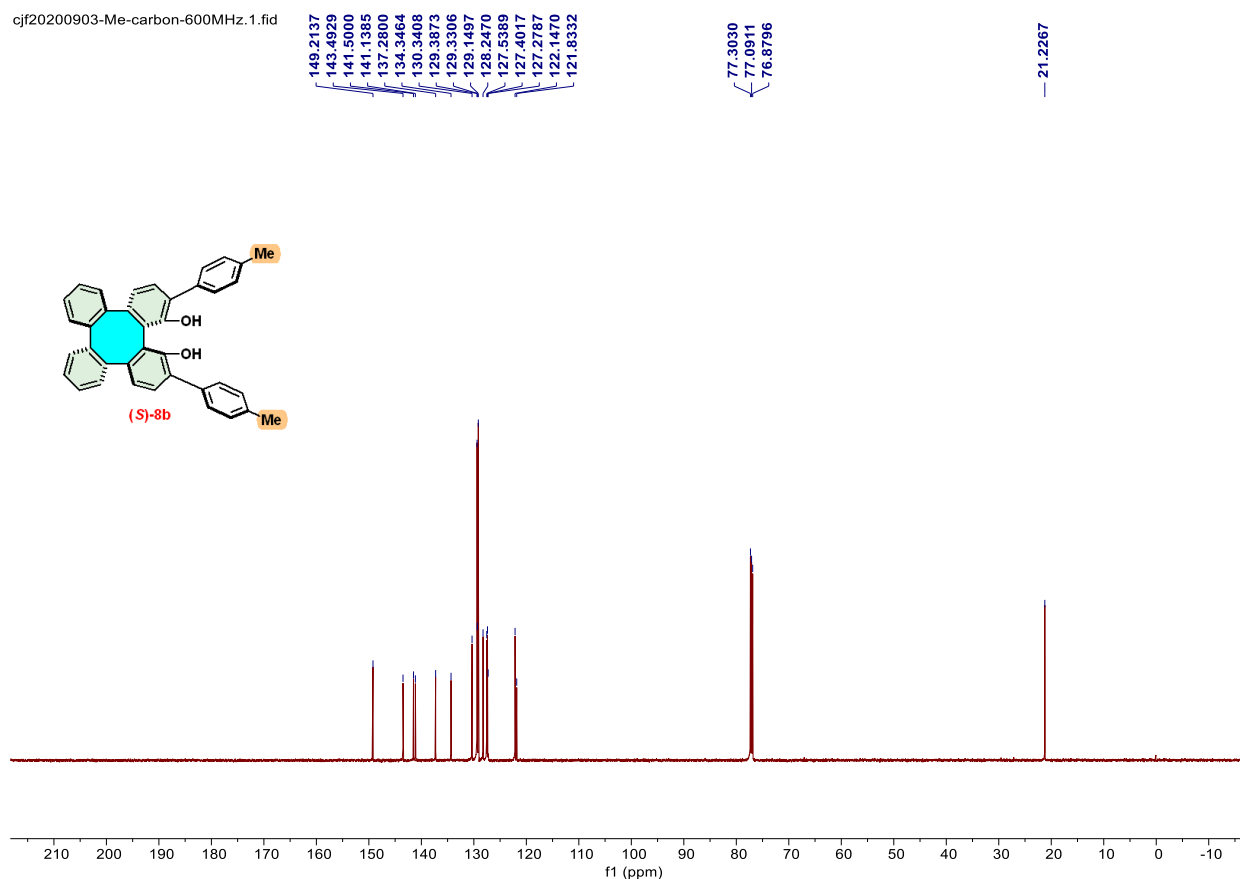


¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8a

SUPPORTING INFORMATION

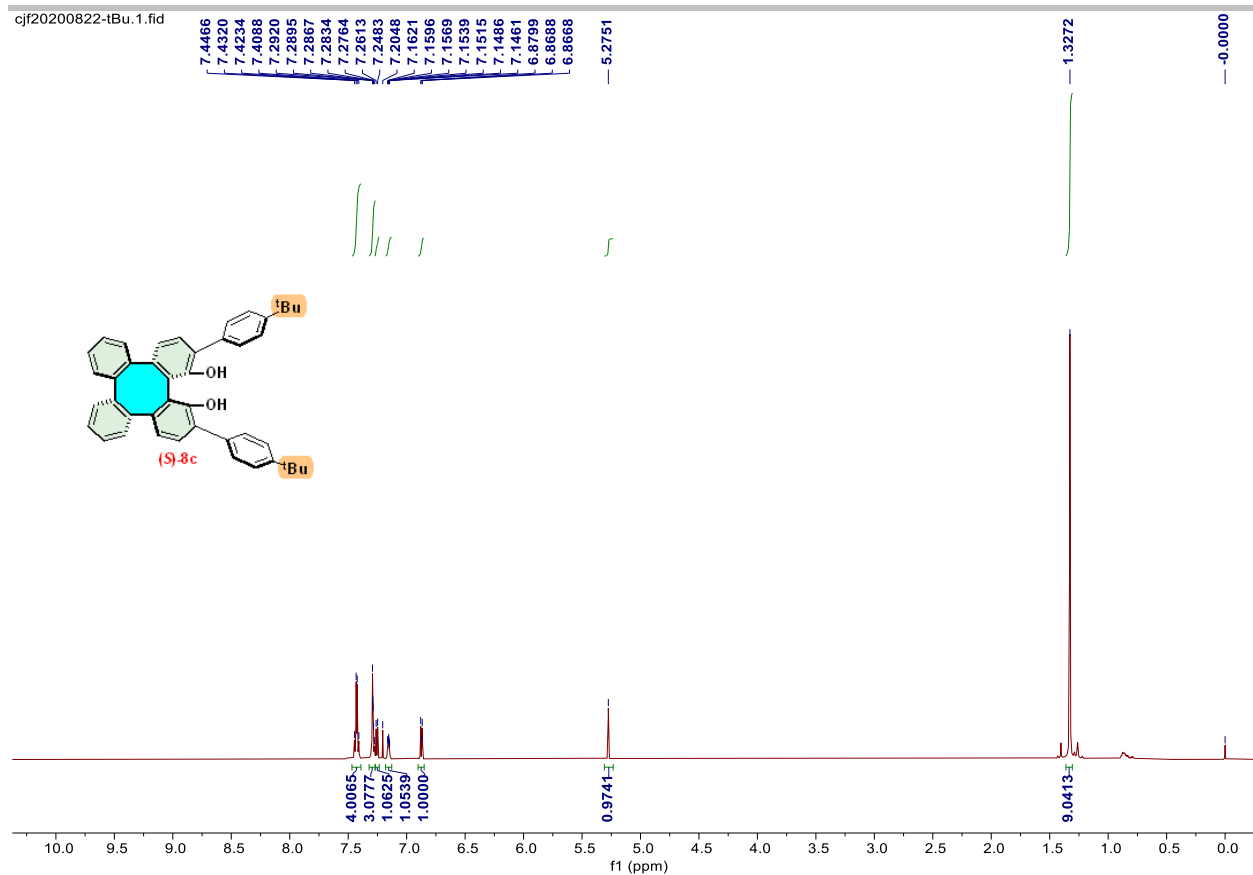


¹H NMR (600 MHz, CDCl₃) spectrum of (S)-8b

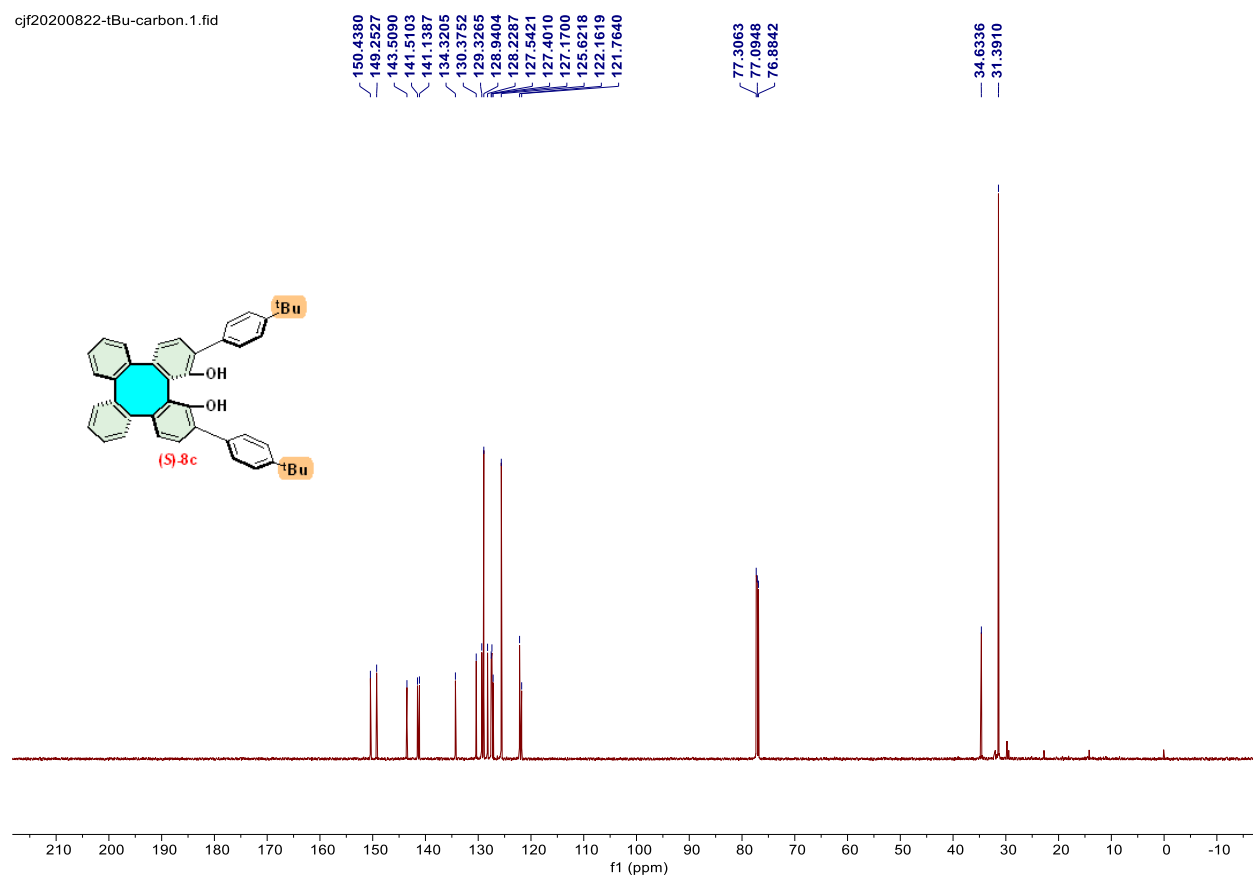


¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8b

SUPPORTING INFORMATION

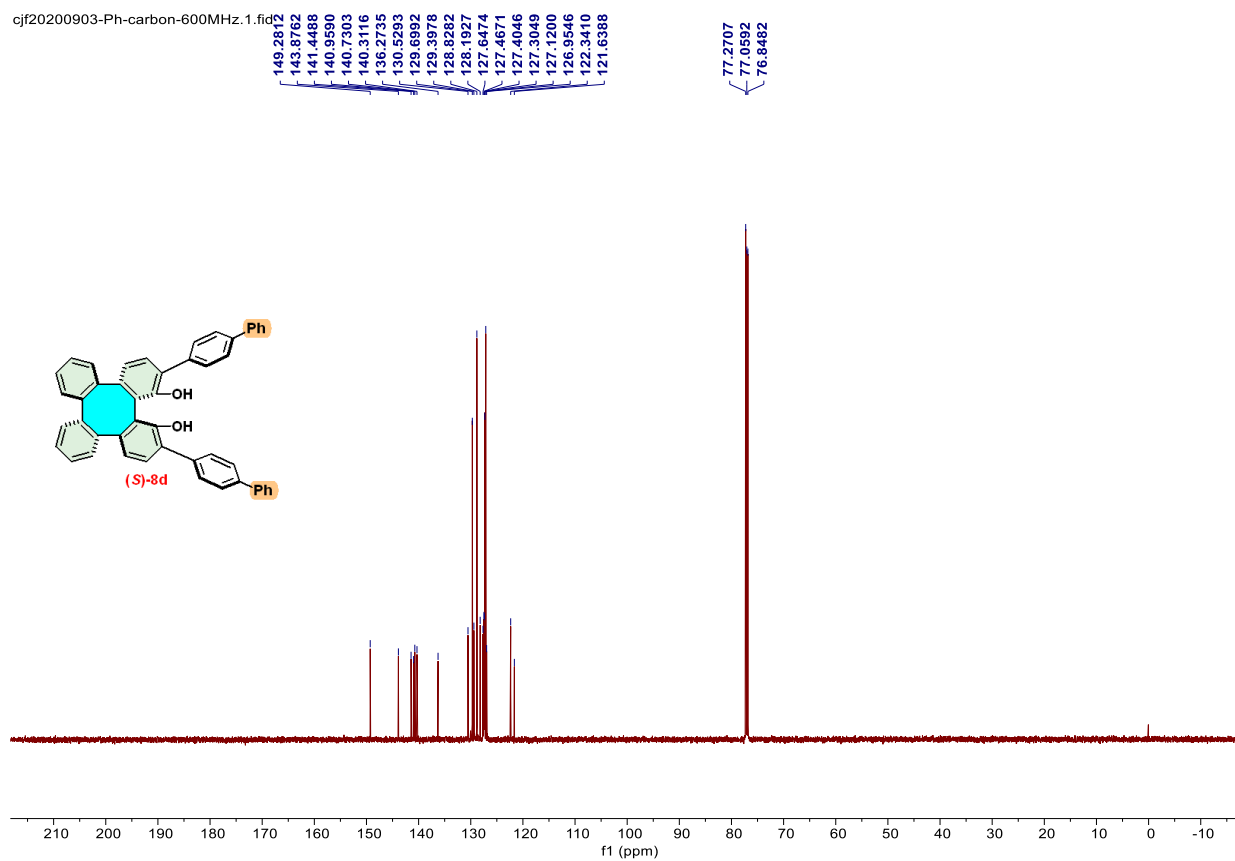
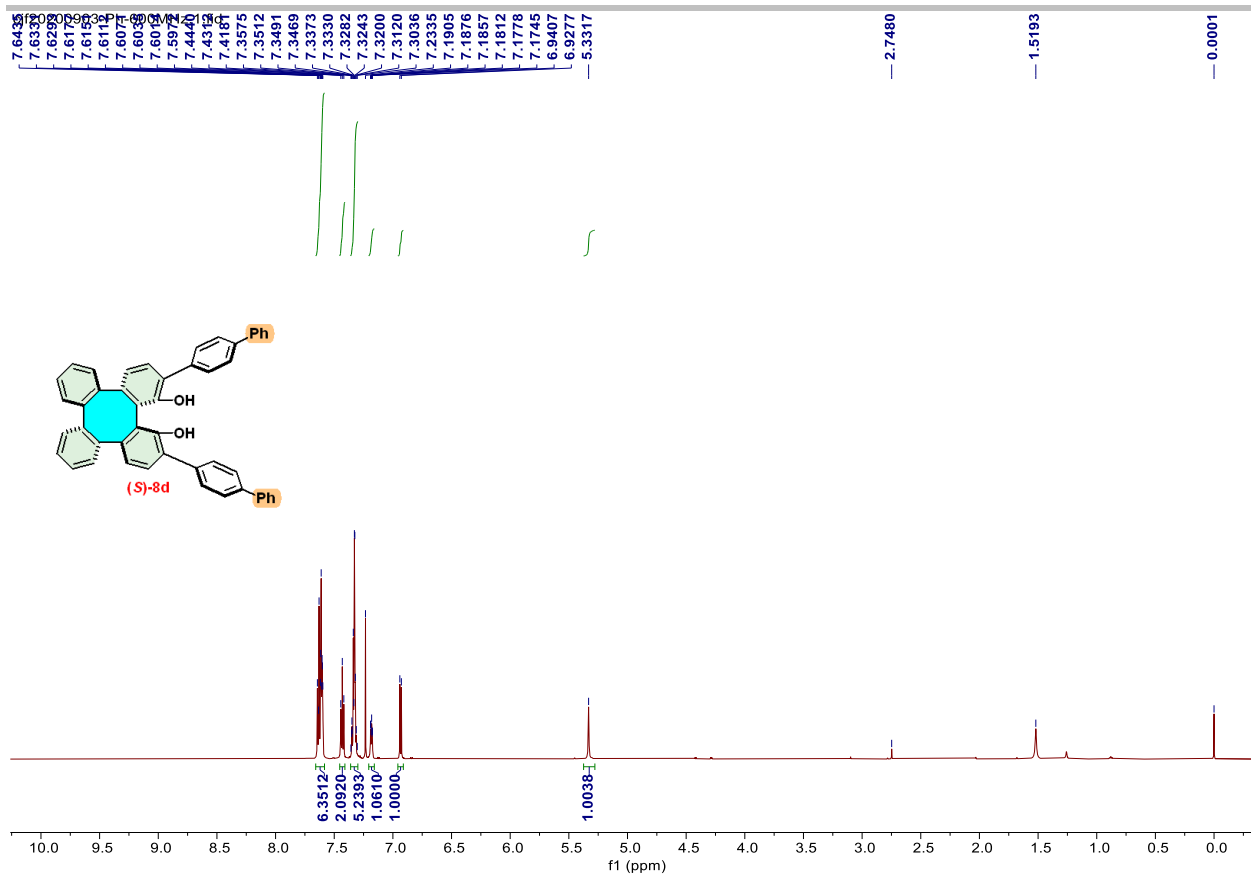


¹H NMR (600 MHz, CDCl₃) spectrum of **(S)-8c**

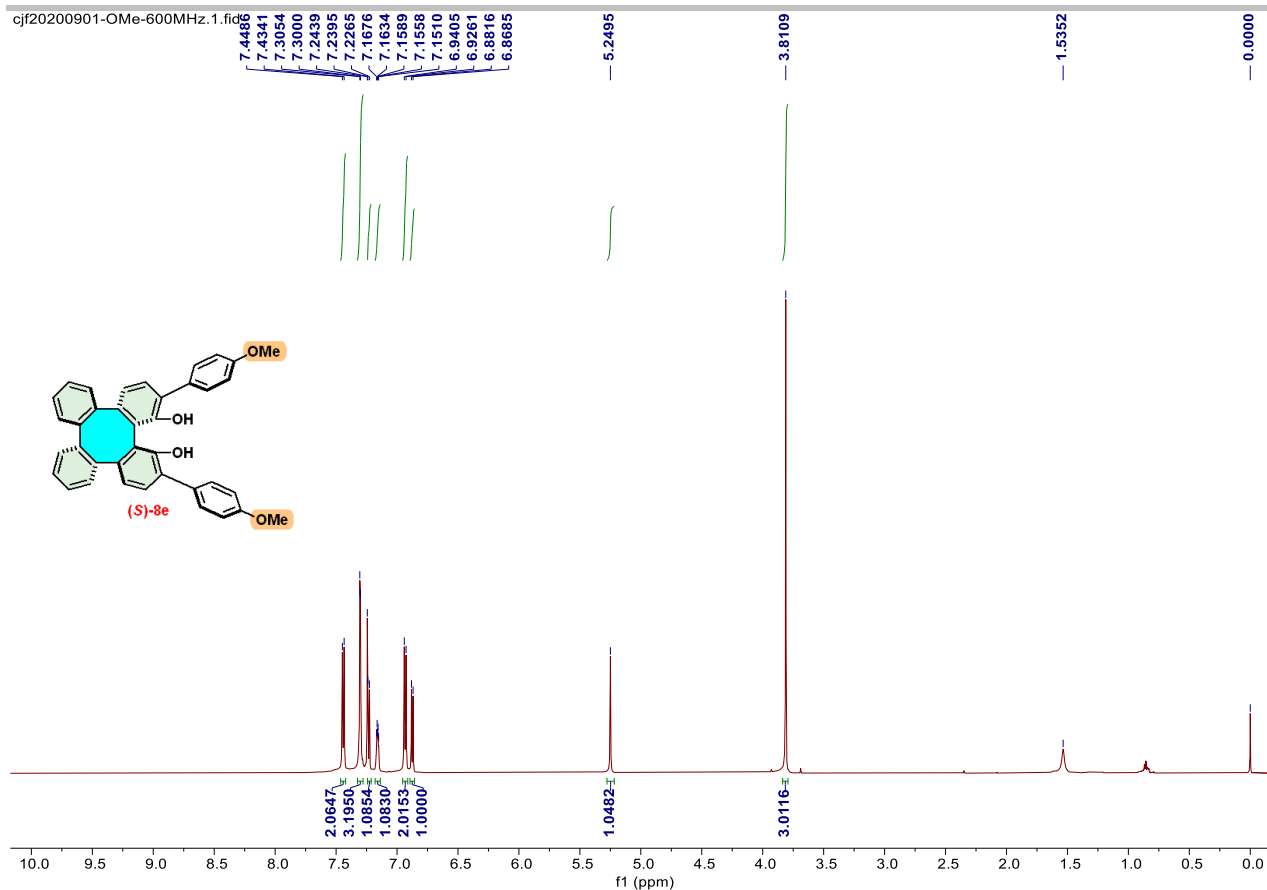


¹³C NMR (150 MHz, CDCl₃) spectrum of **(S)-8c**

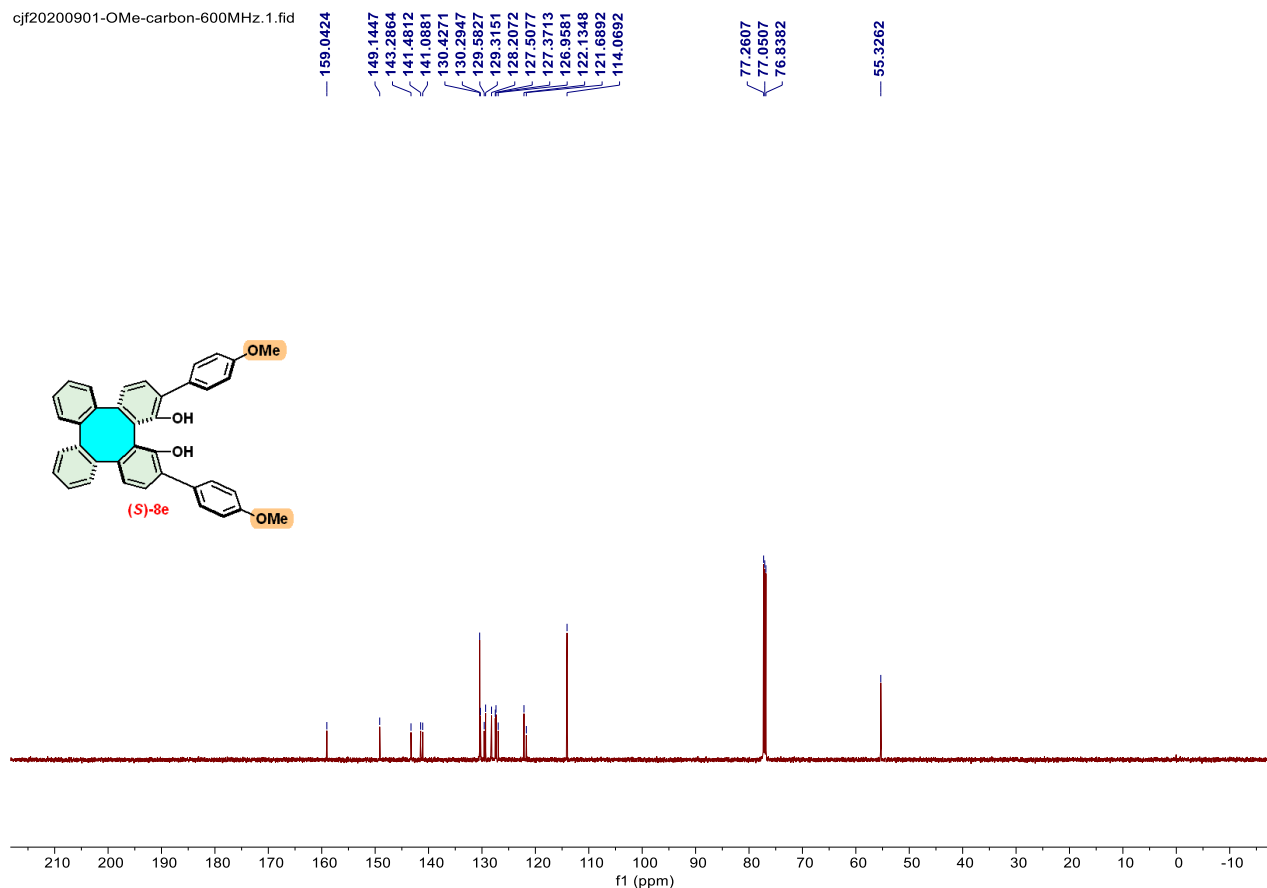
SUPPORTING INFORMATION



SUPPORTING INFORMATION



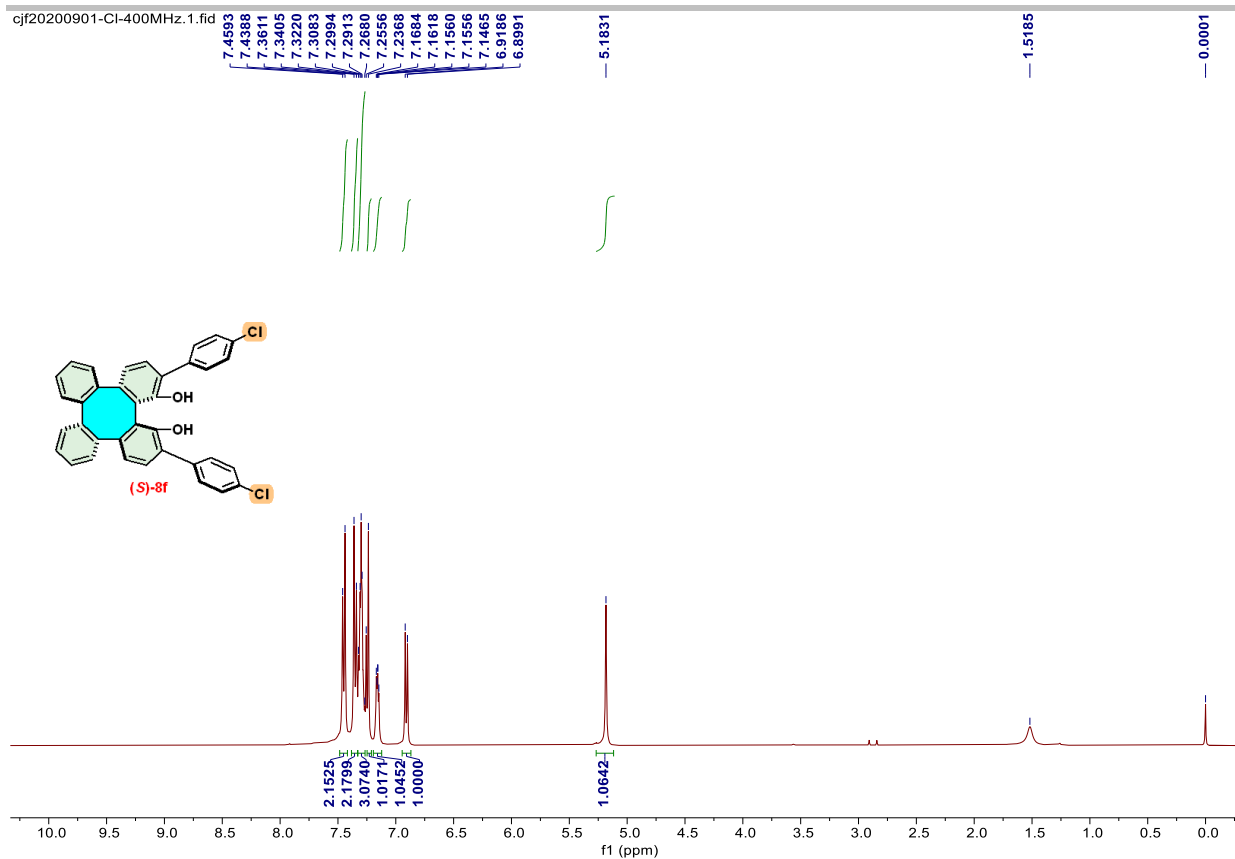
¹H NMR (600 MHz, CDCl₃) spectrum of (S)-8e



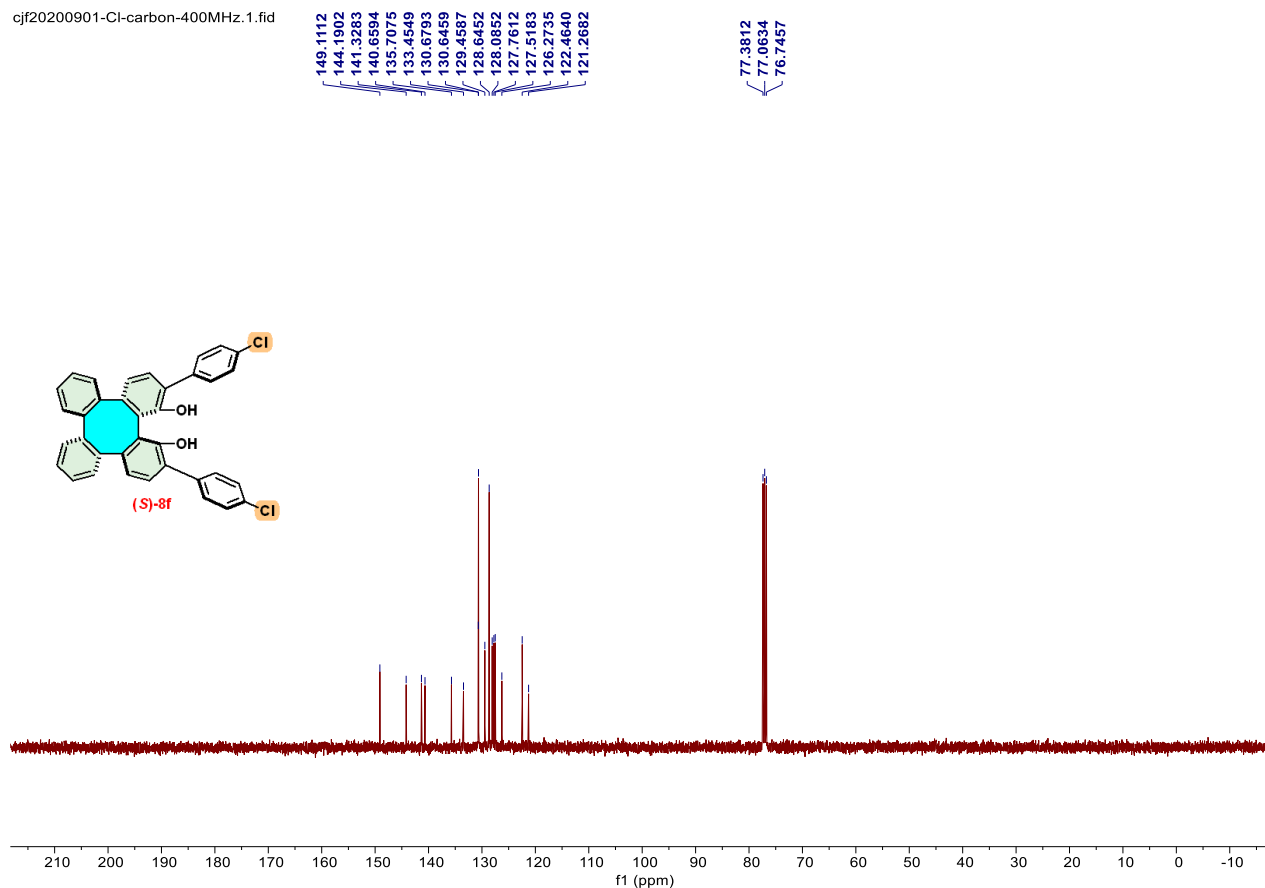
¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8e

SUPPORTING INFORMATION

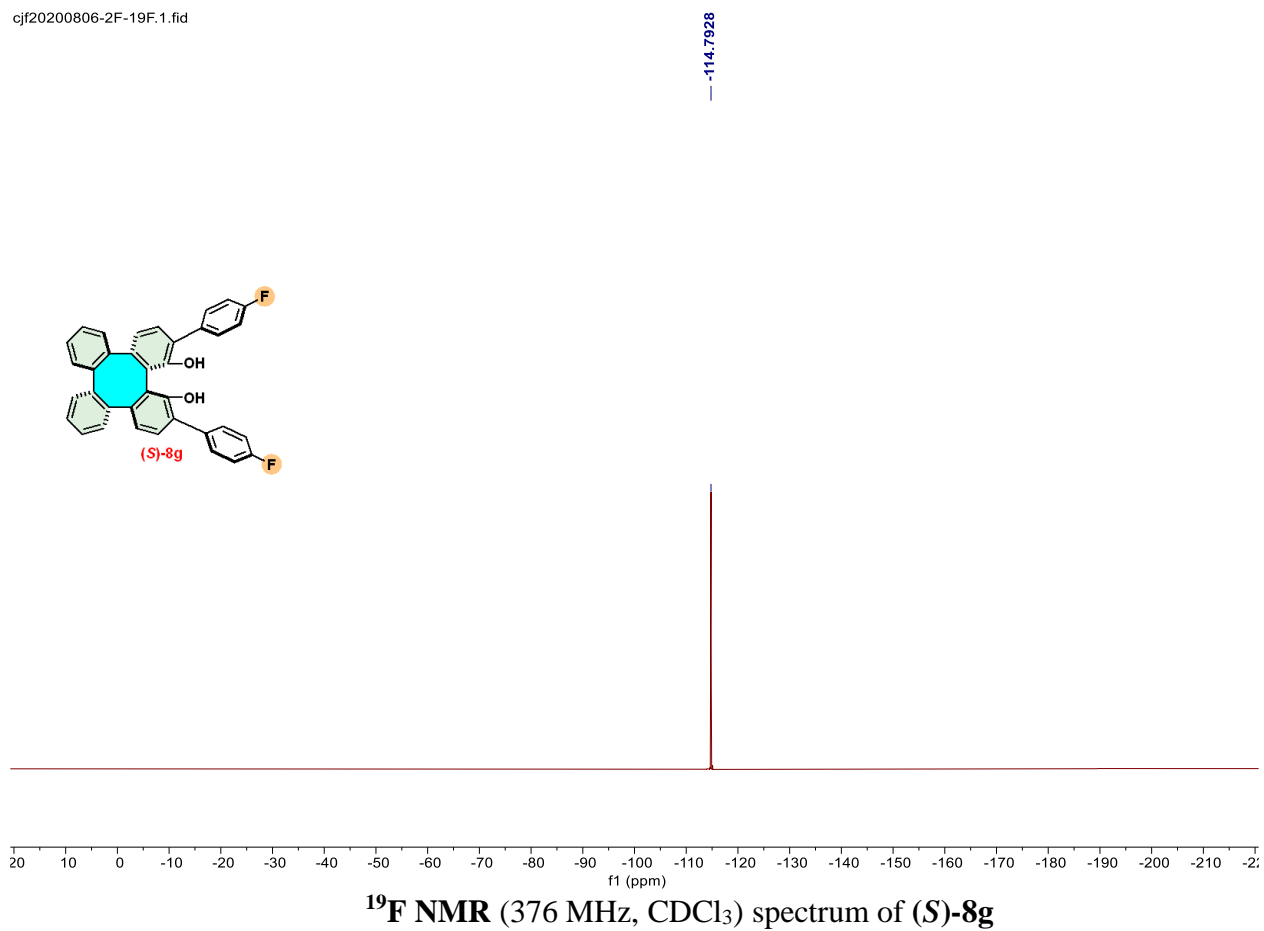
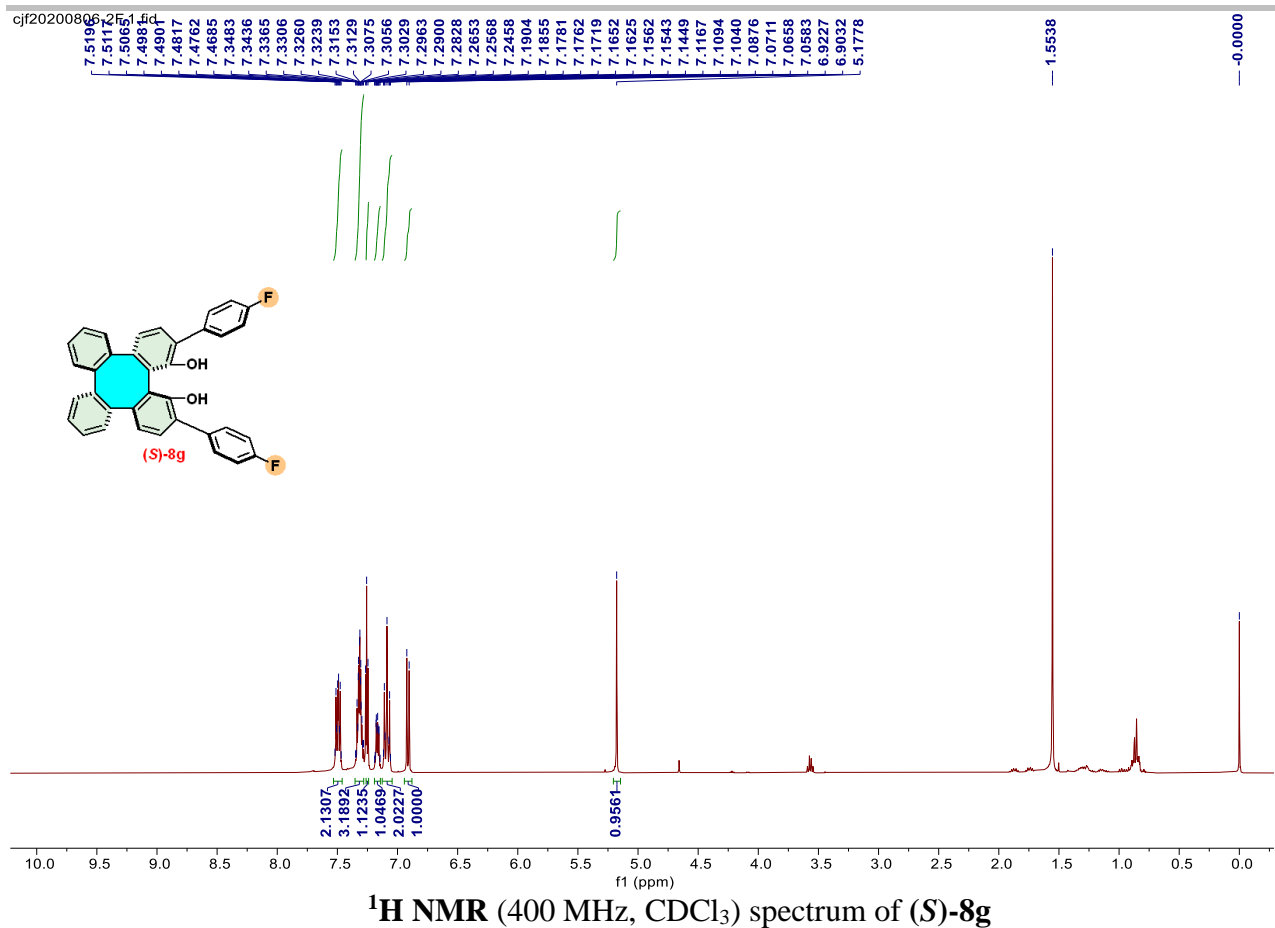
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cfj20200901-Cl-carbon-400MHz.1.fid



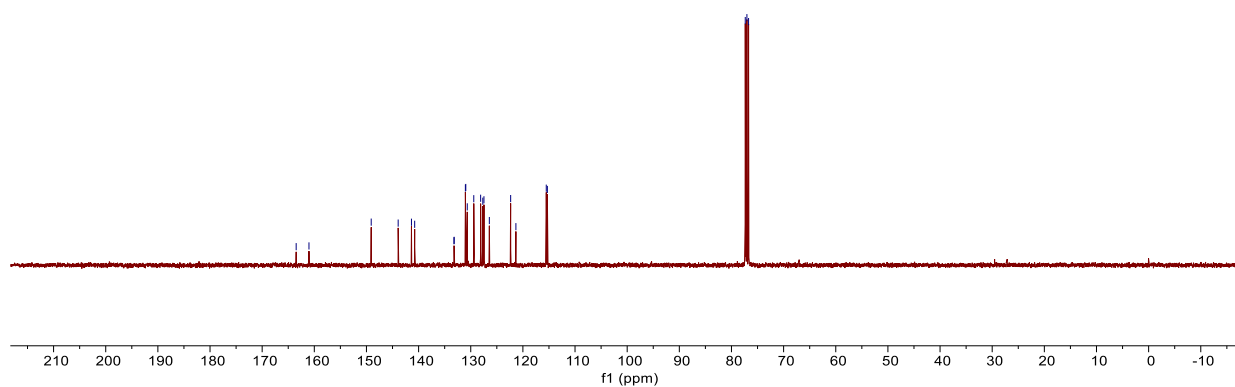
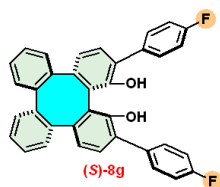
SUPPORTING INFORMATION



SUPPORTING INFORMATION

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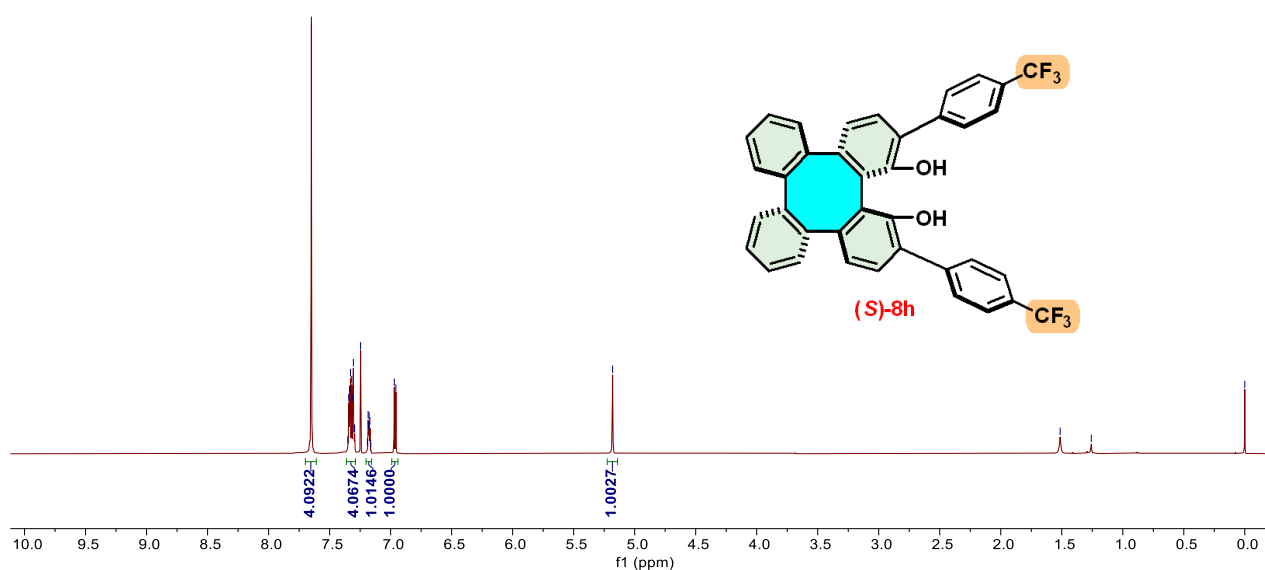
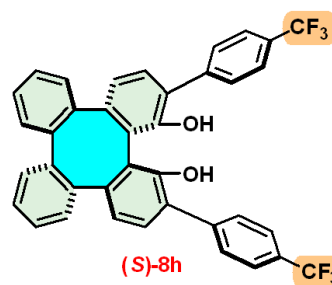
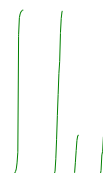
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122.3475
121.3409
115.5176
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76.7215



^{13}C NMR (100 MHz, CDCl_3) spectrum of **(S)-8g**

cfj20200829-CF3.1.fid

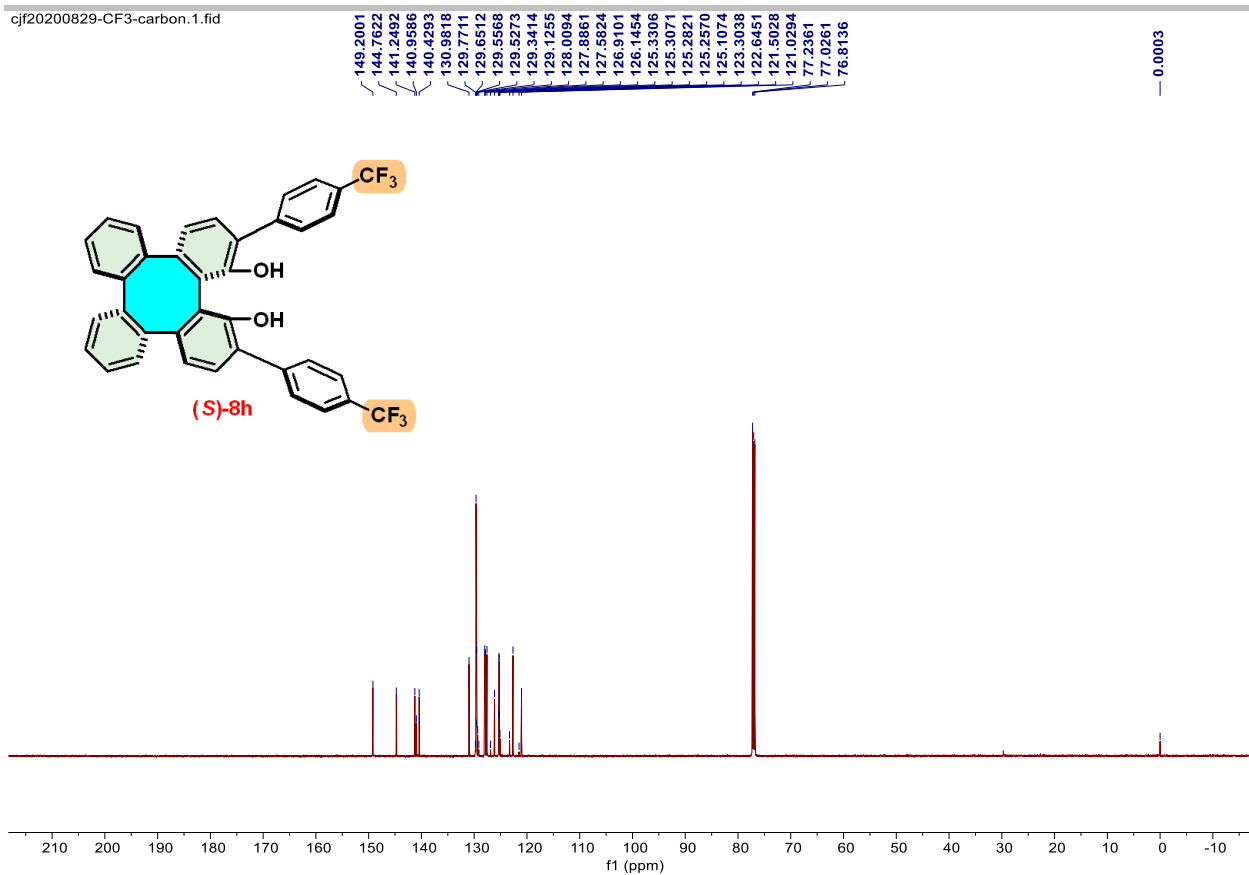
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7.1901
7.1845
7.1804
7.1760
7.1696
7.1627
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^1H NMR (600 MHz, CDCl_3) spectrum of **(S)-8h**

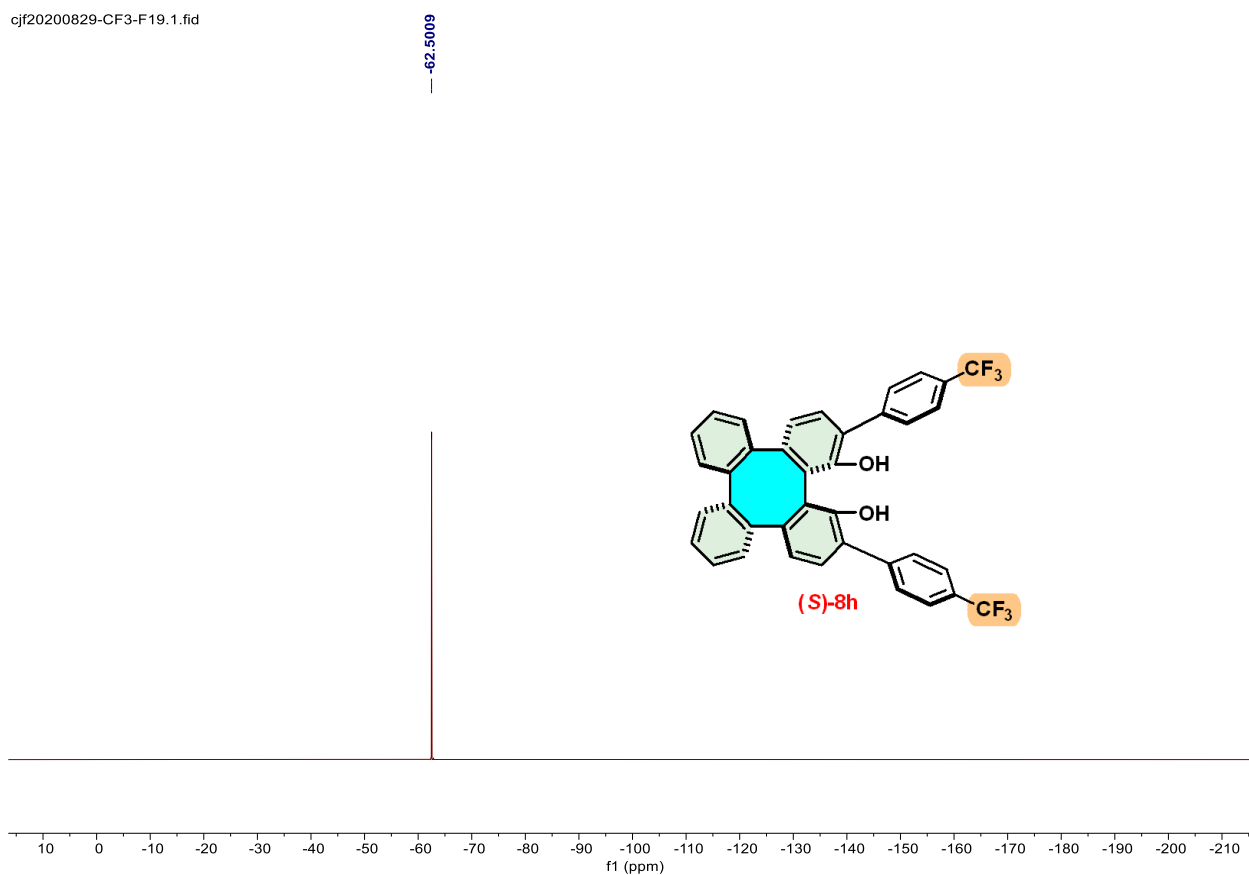
SUPPORTING INFORMATION

cfj20200829-CF3-carbon.1.fid



¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8h

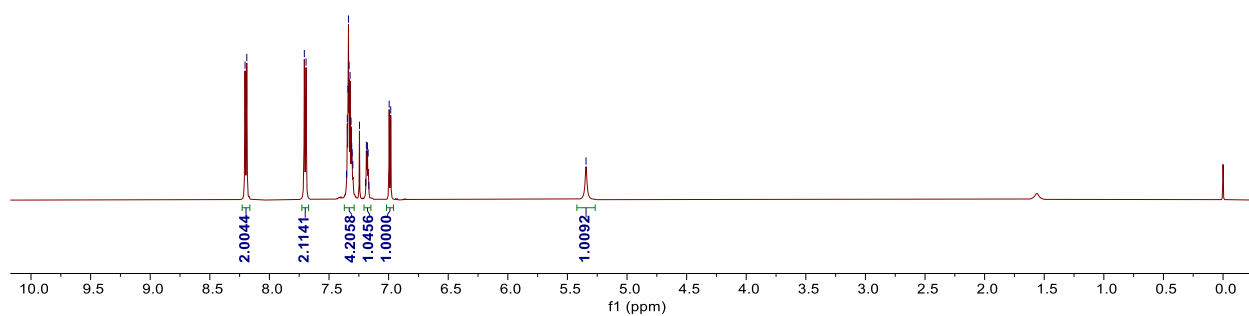
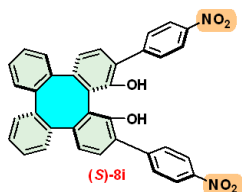
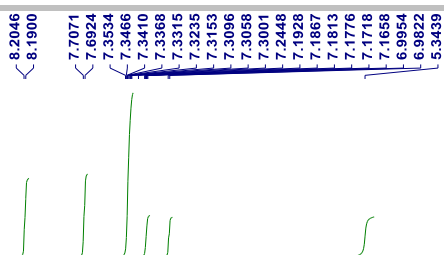
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¹⁹F NMR (565 MHz, CDCl₃) spectrum of (S)-8h

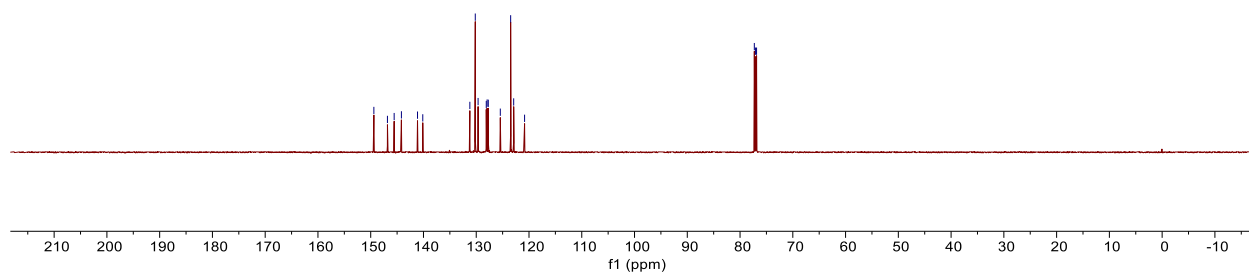
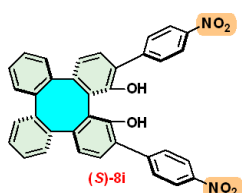
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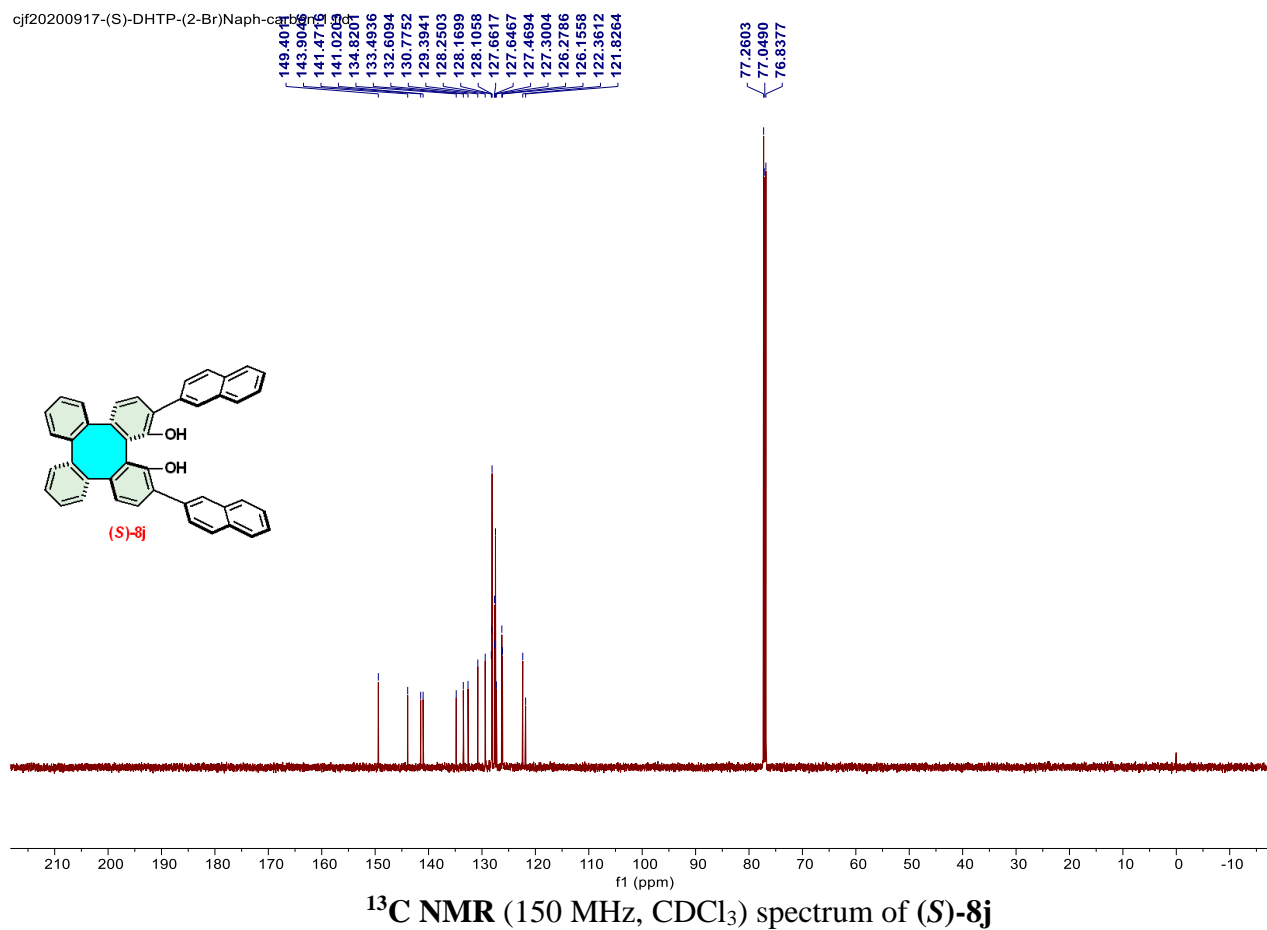
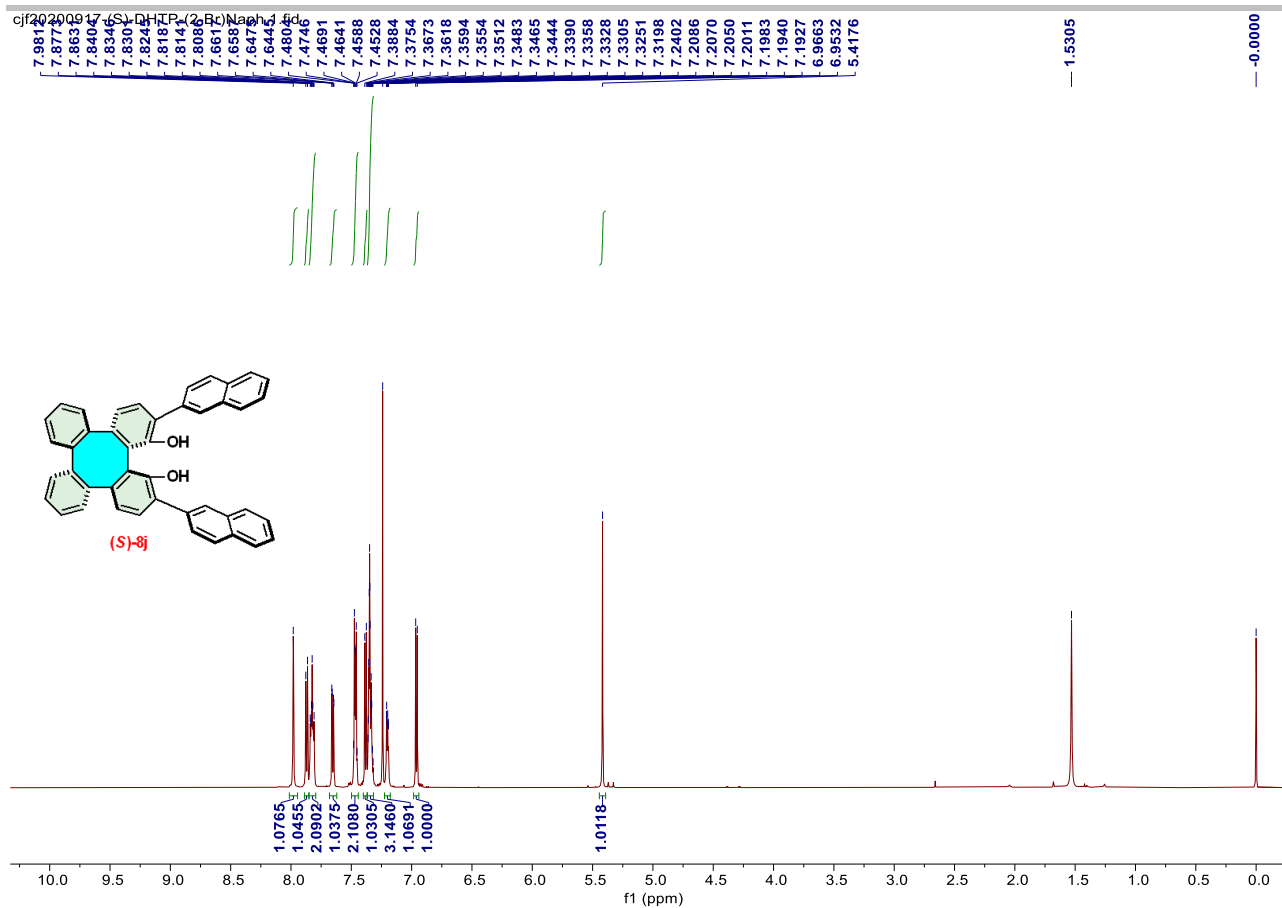
¹H NMR (600 MHz, CDCl₃) spectrum of (S)-8i

cfj20200831-NO2-carbon.1.fid

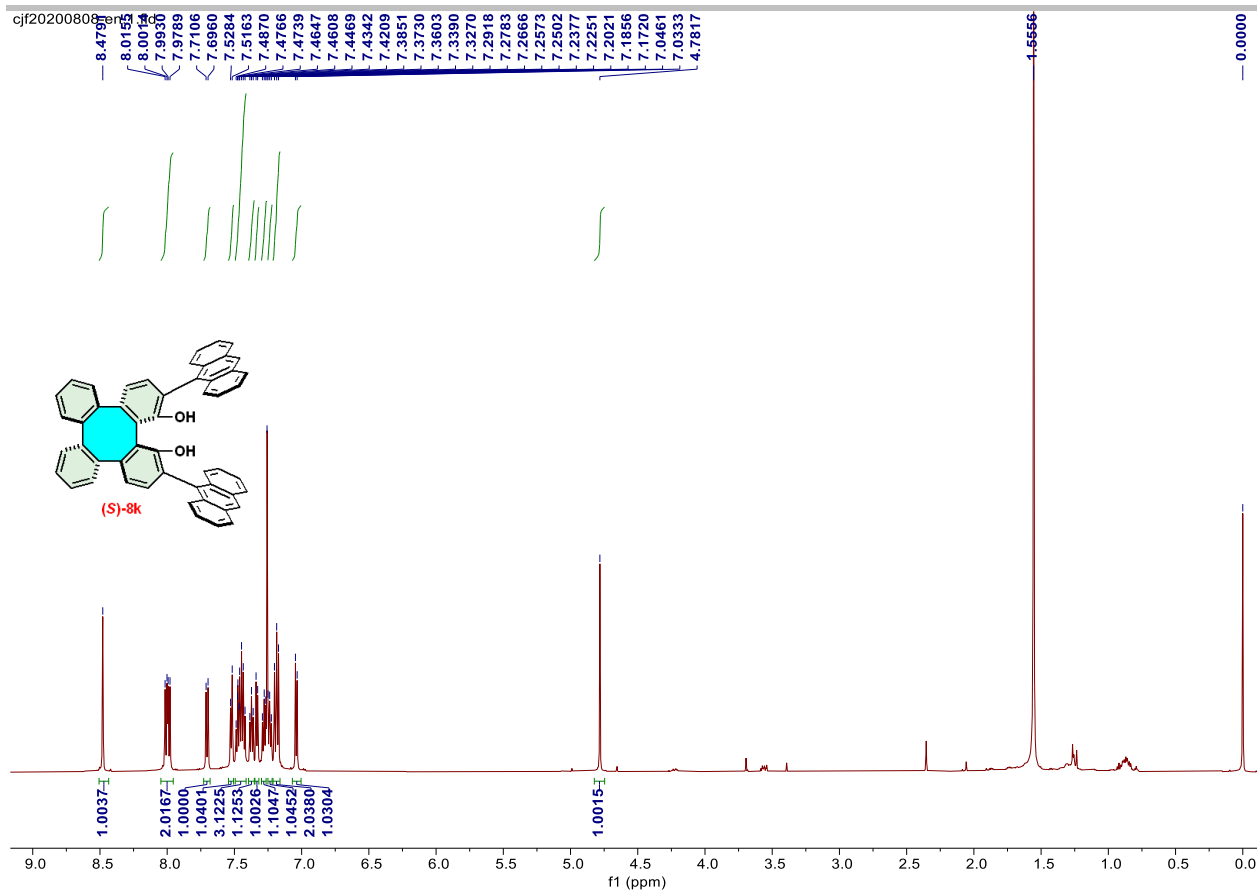


¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8i

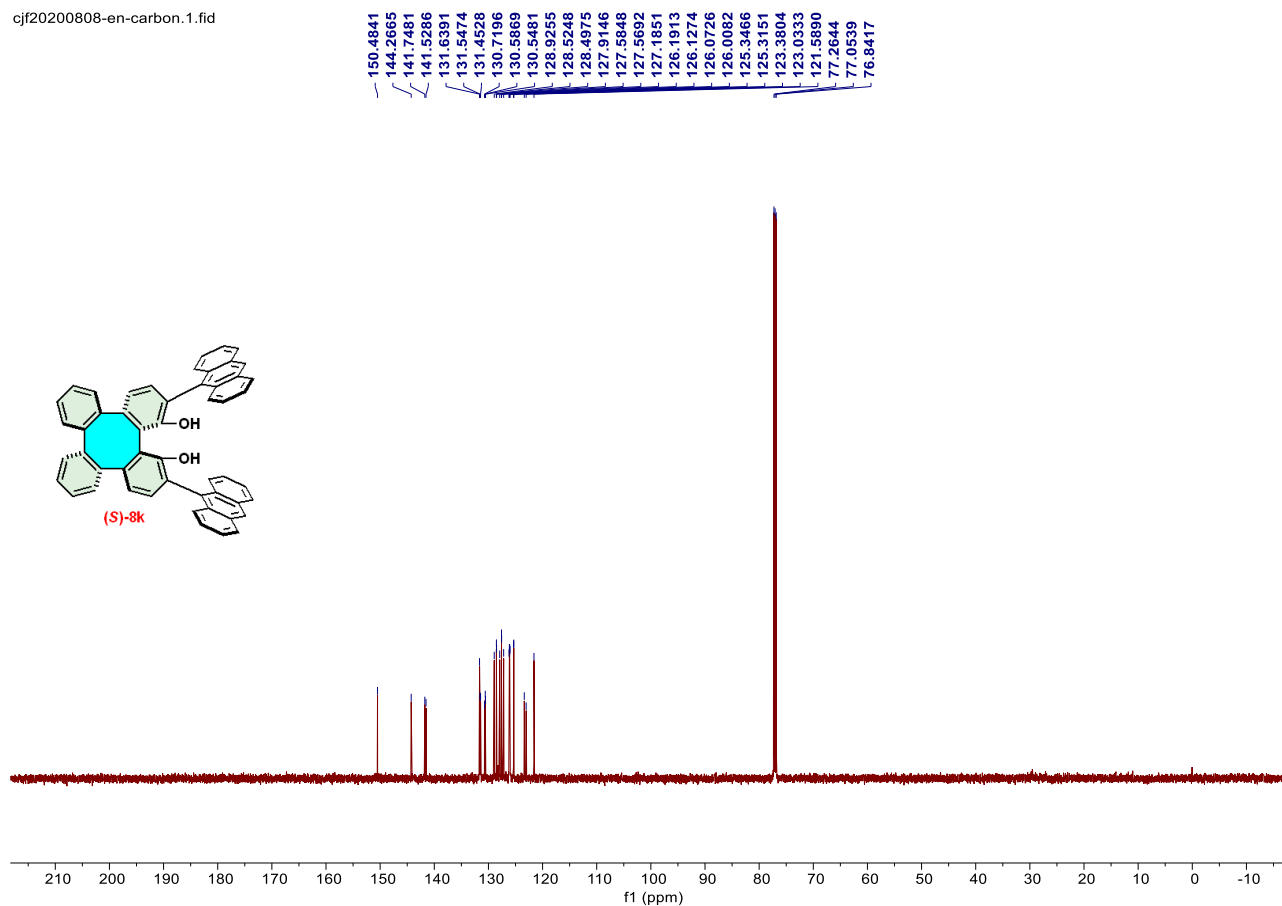
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SUPPORTING INFORMATION

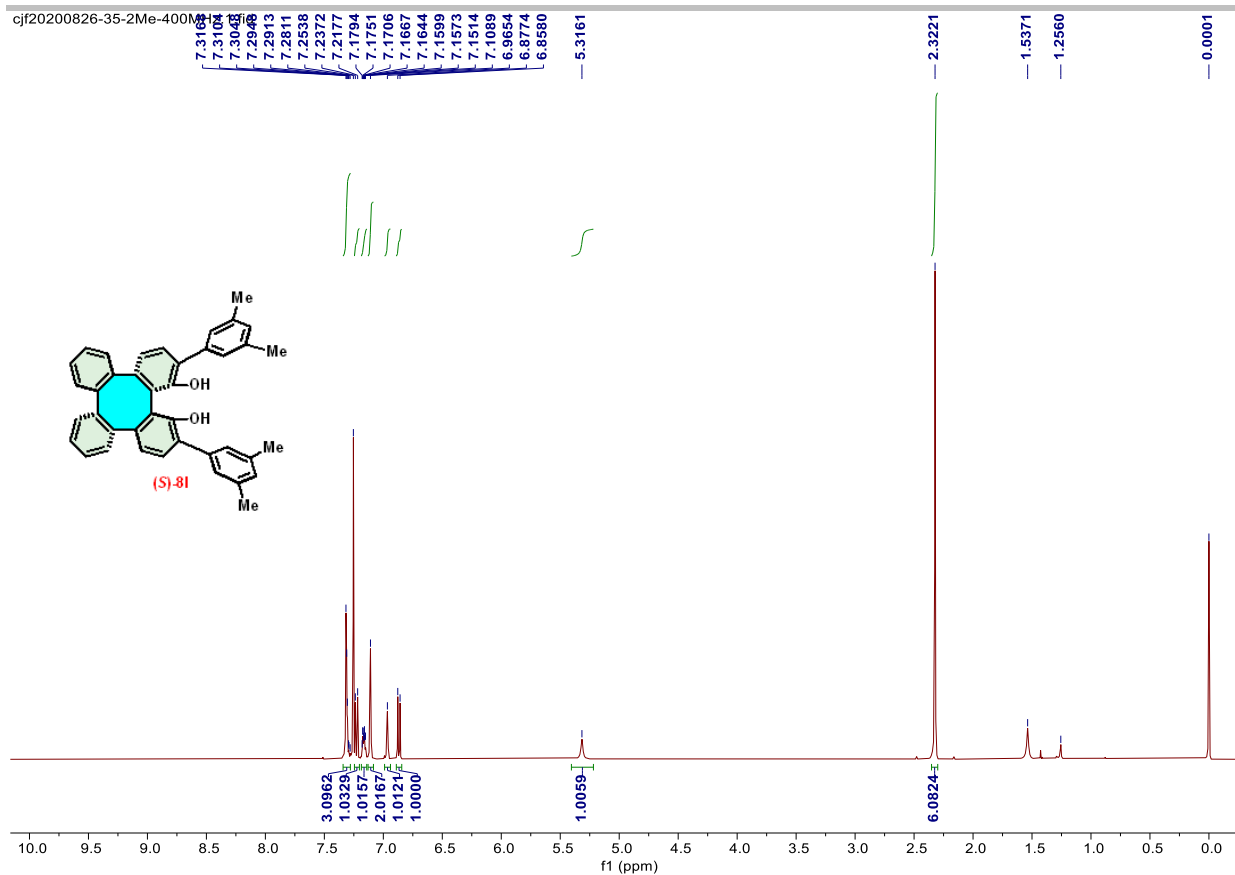


¹H NMR (600 MHz, CDCl₃) spectrum of (S)-8k

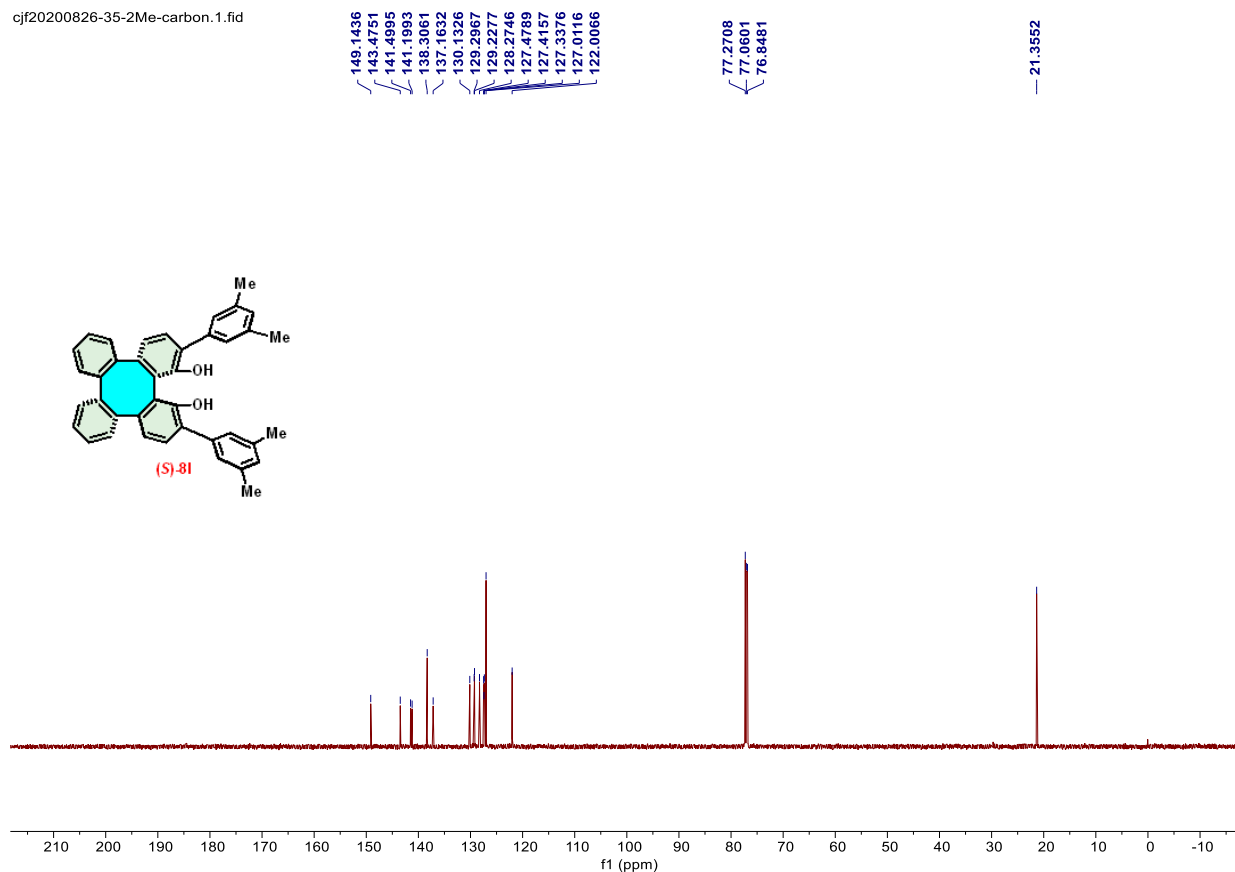


¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8k

SUPPORTING INFORMATION

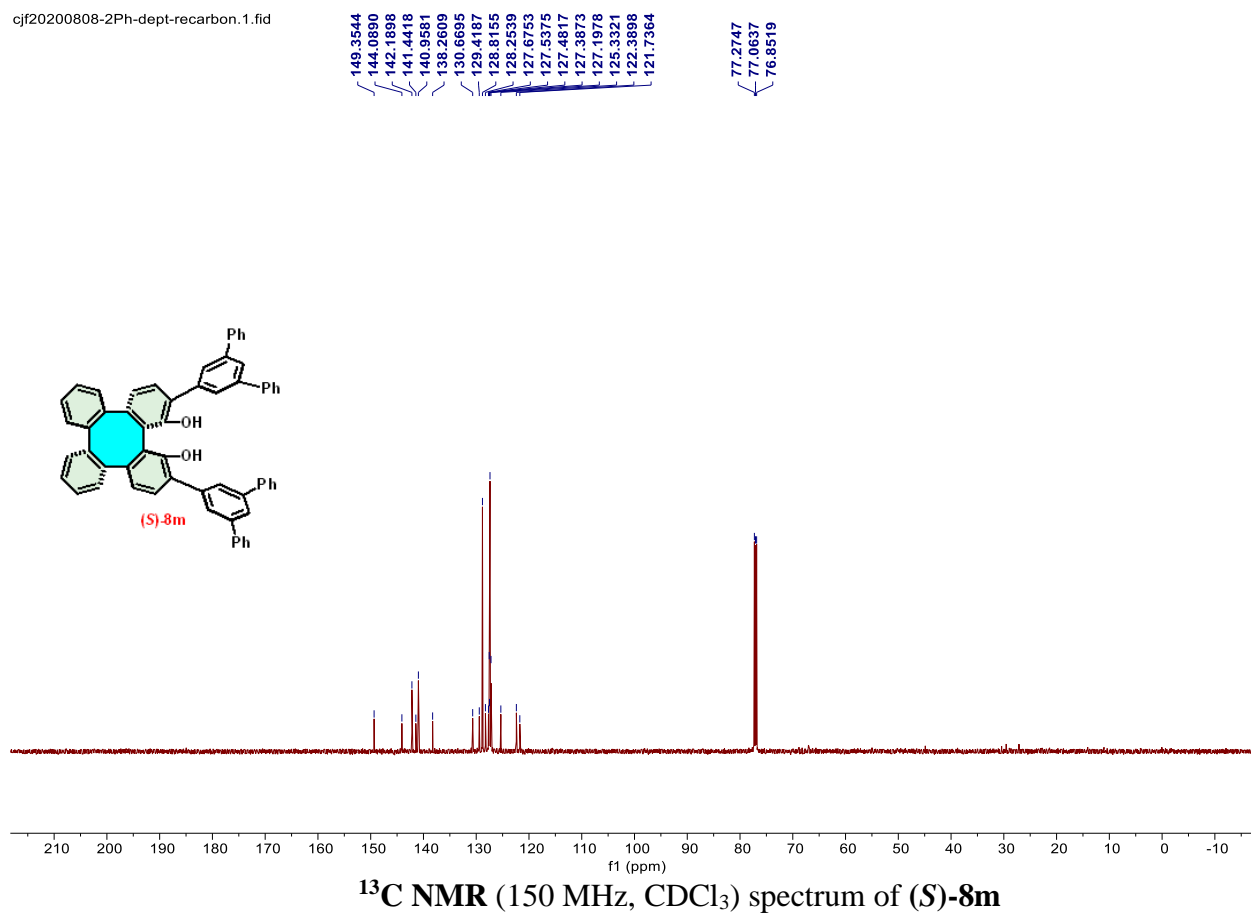
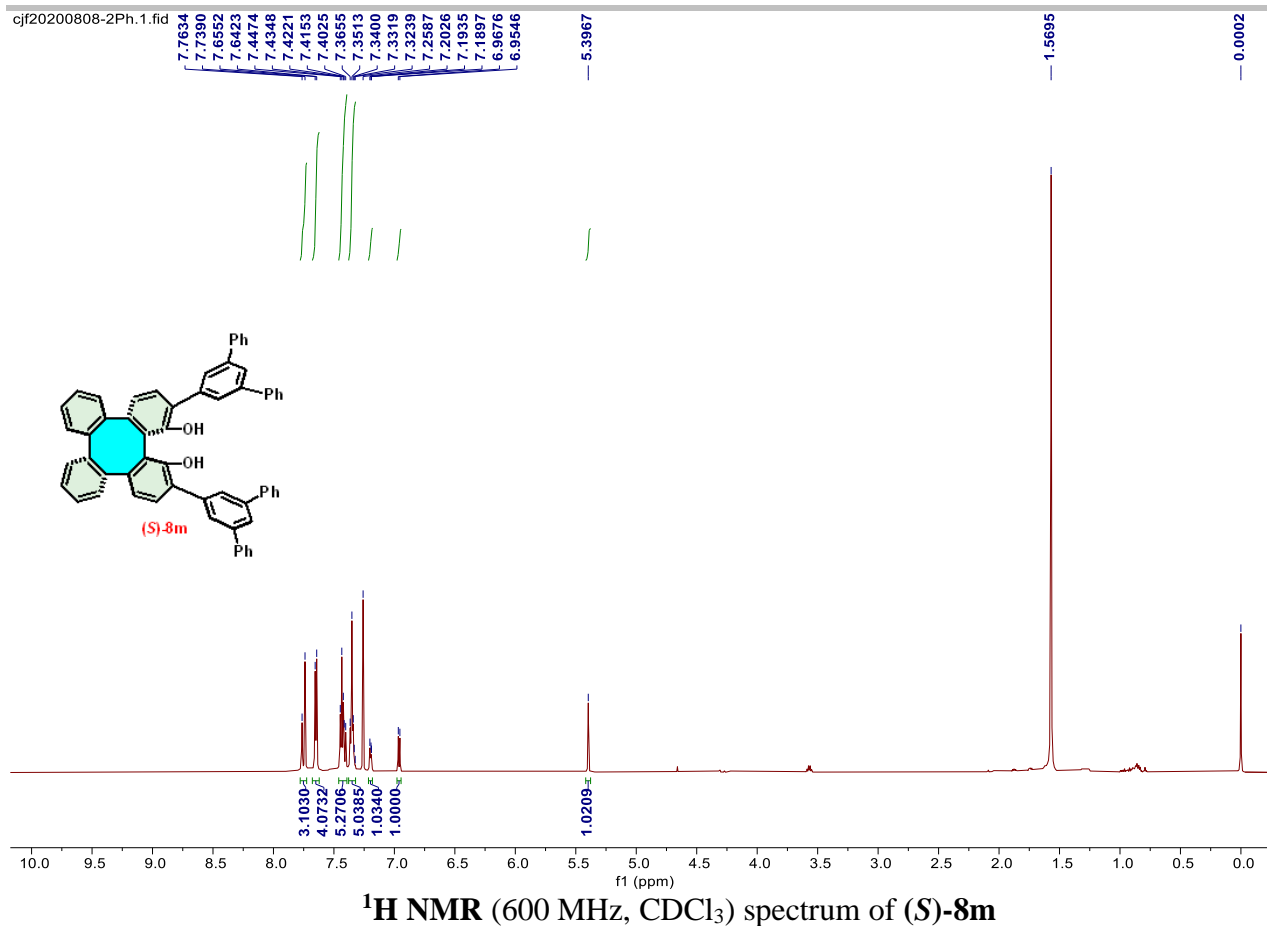


¹H NMR (400 MHz, CDCl₃) spectrum of (S)-8I

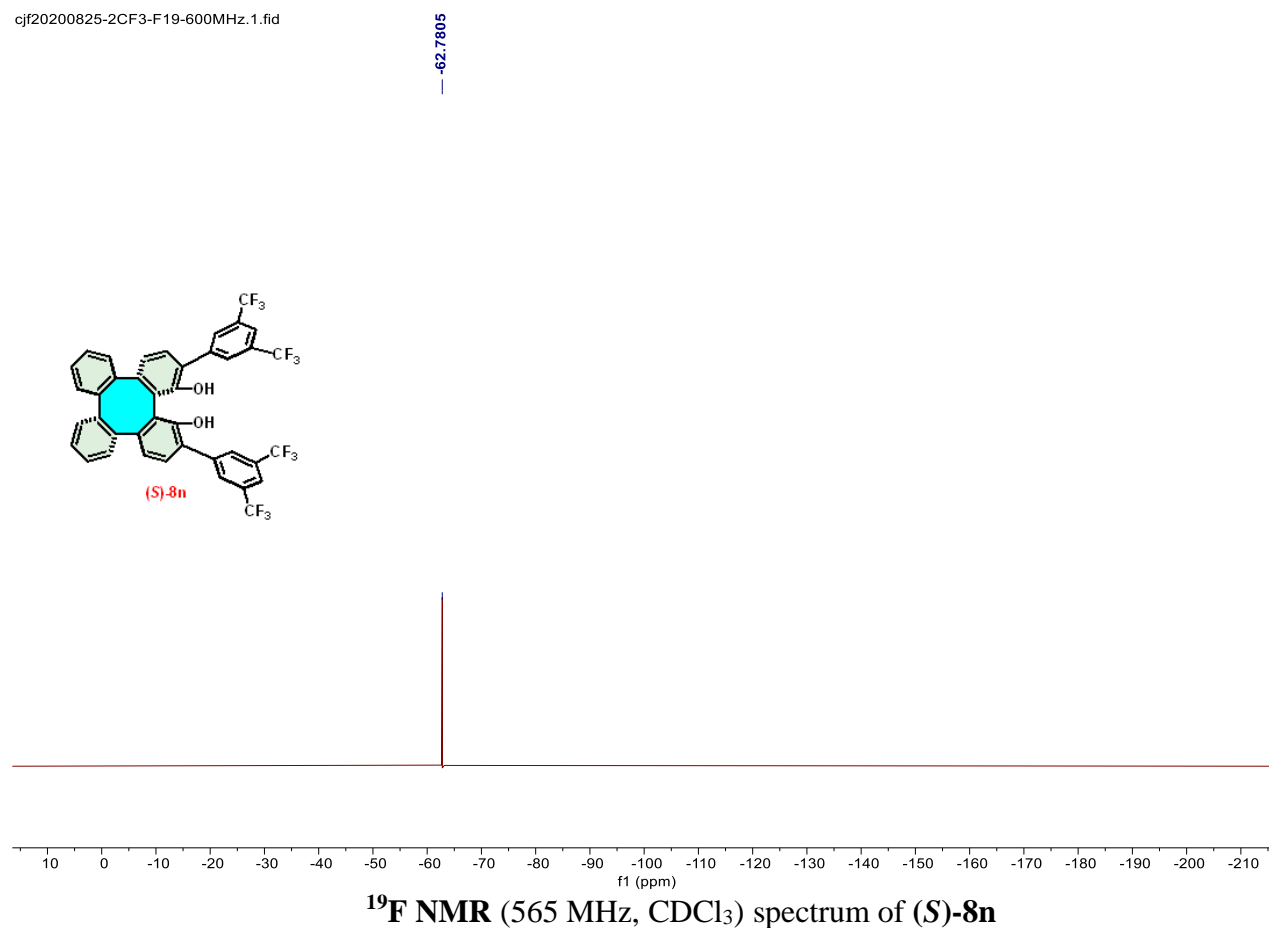
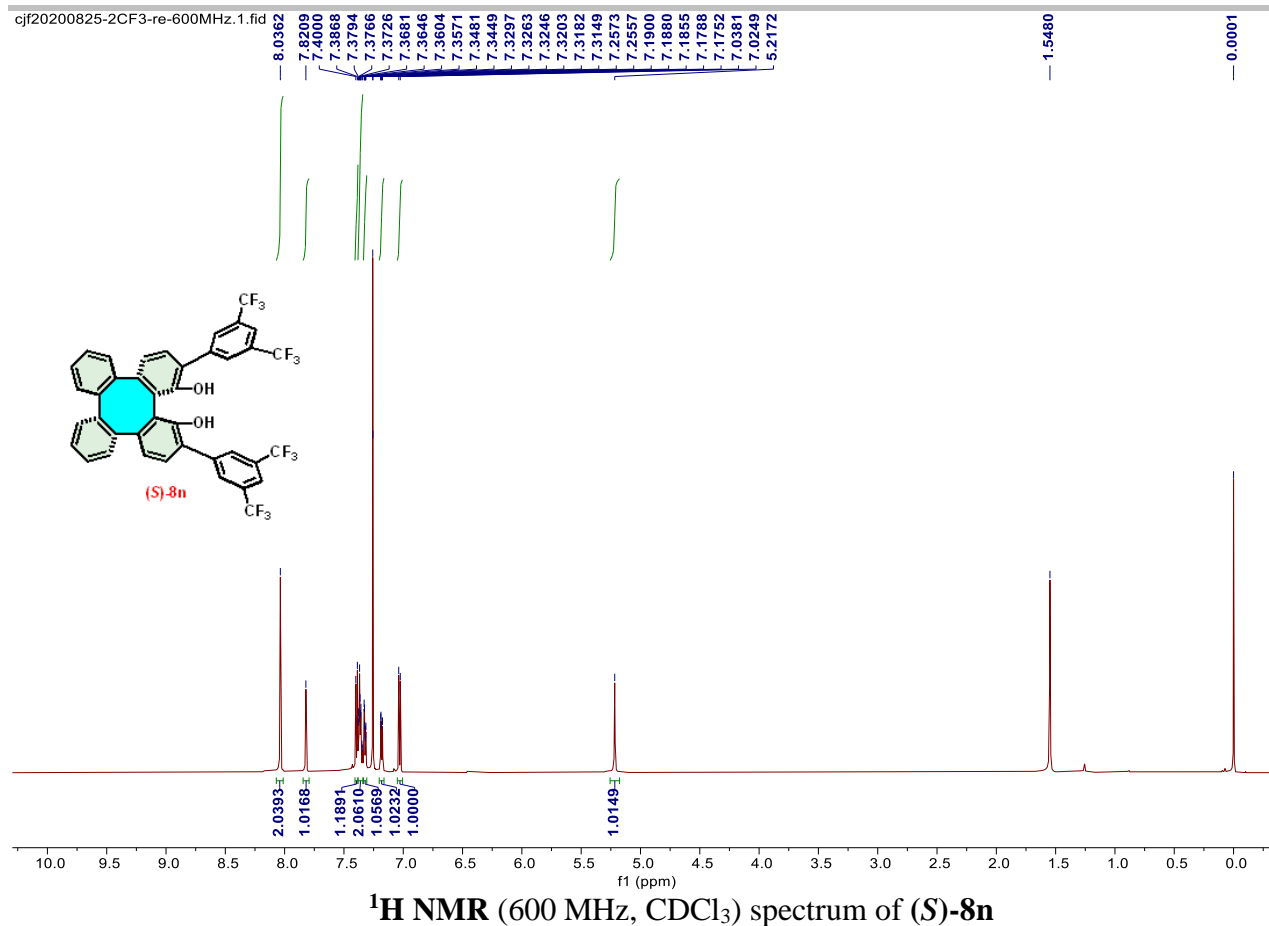


¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8I

SUPPORTING INFORMATION

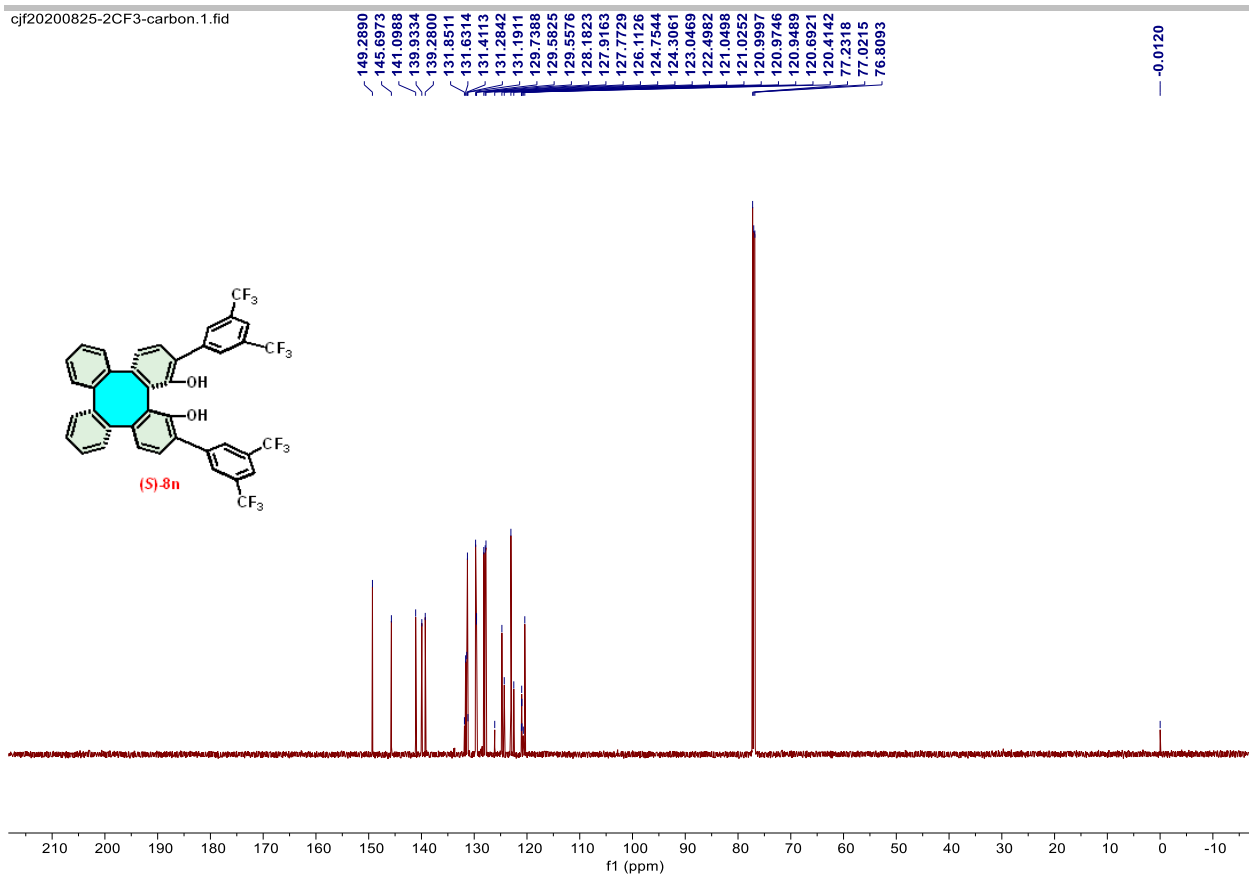


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SUPPORTING INFORMATION

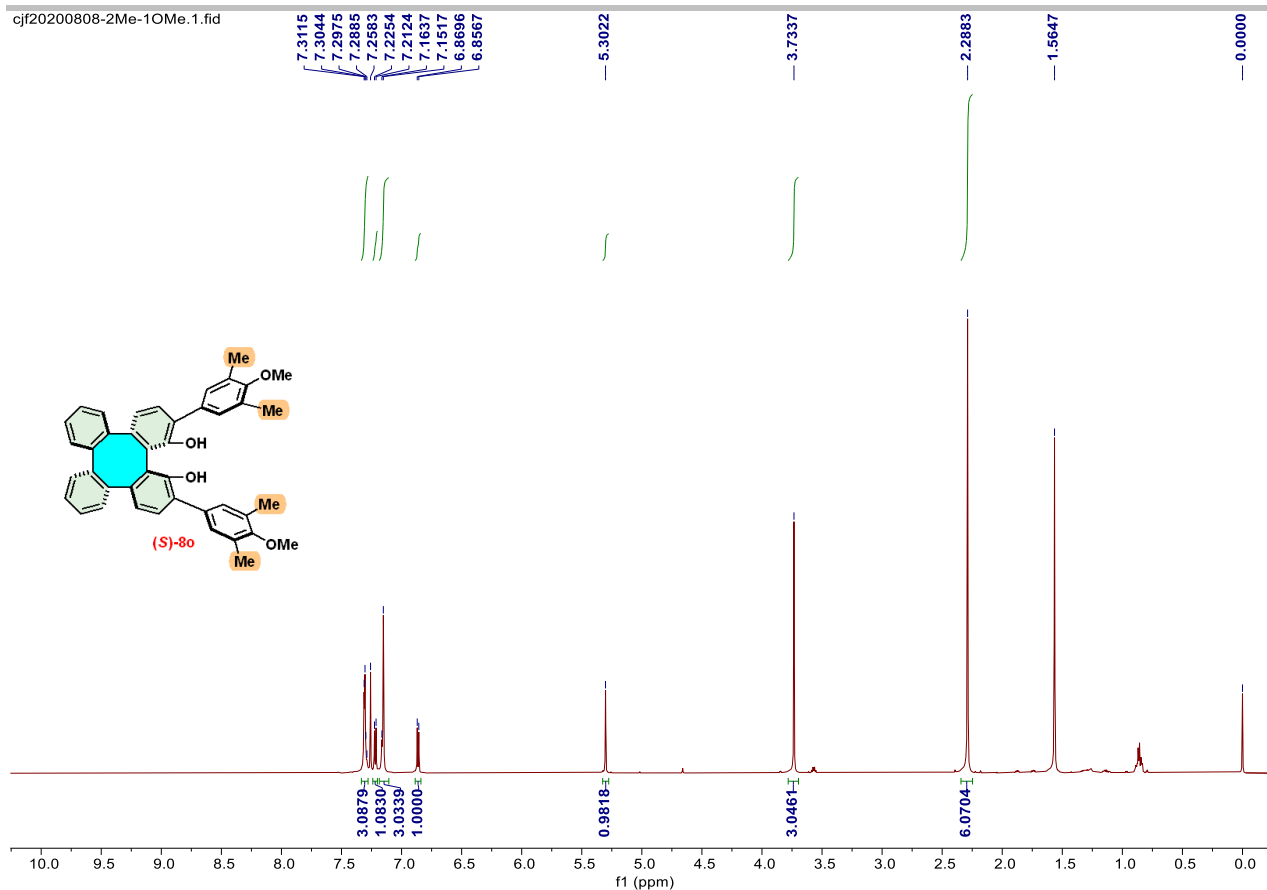
cj20200825-2CF3-carbon.1.fid



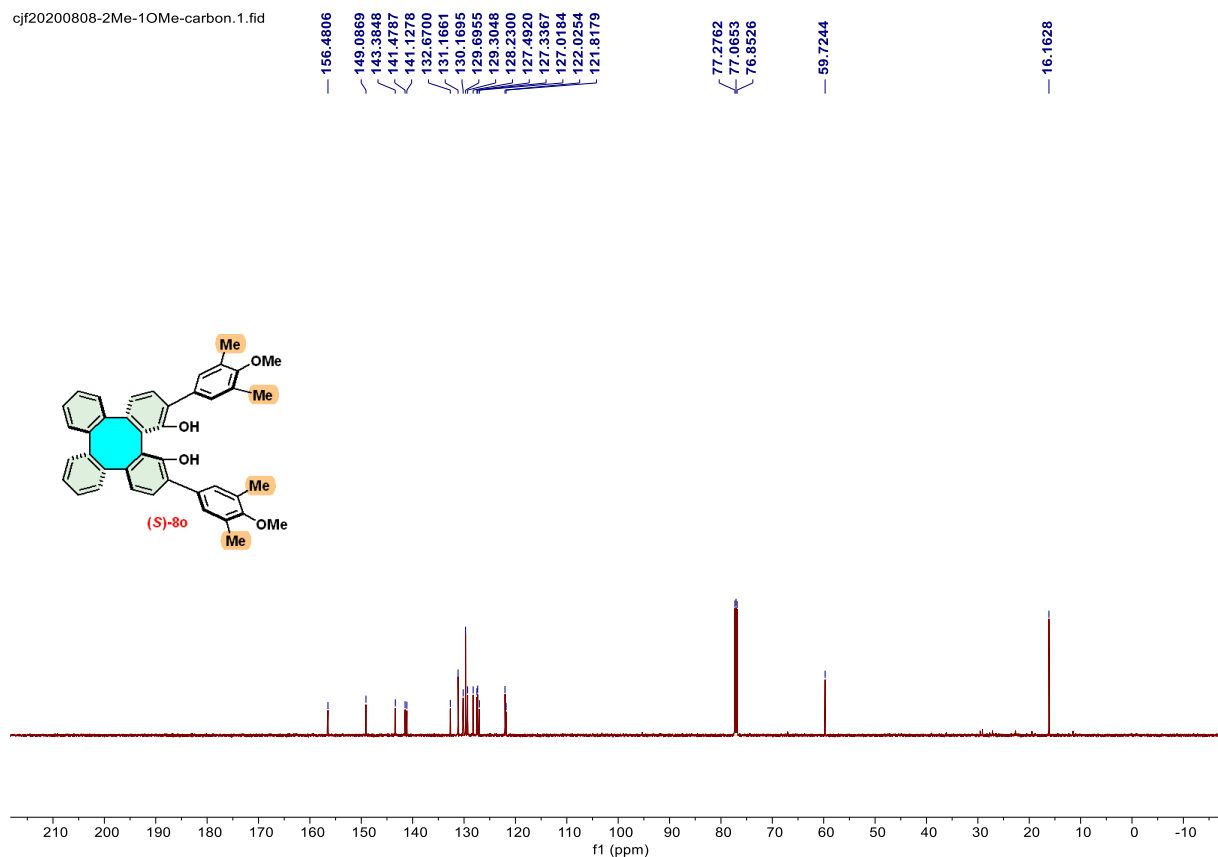
^{13}C NMR (150 MHz, CDCl_3) spectrum of (S)-8n

SUPPORTING INFORMATION

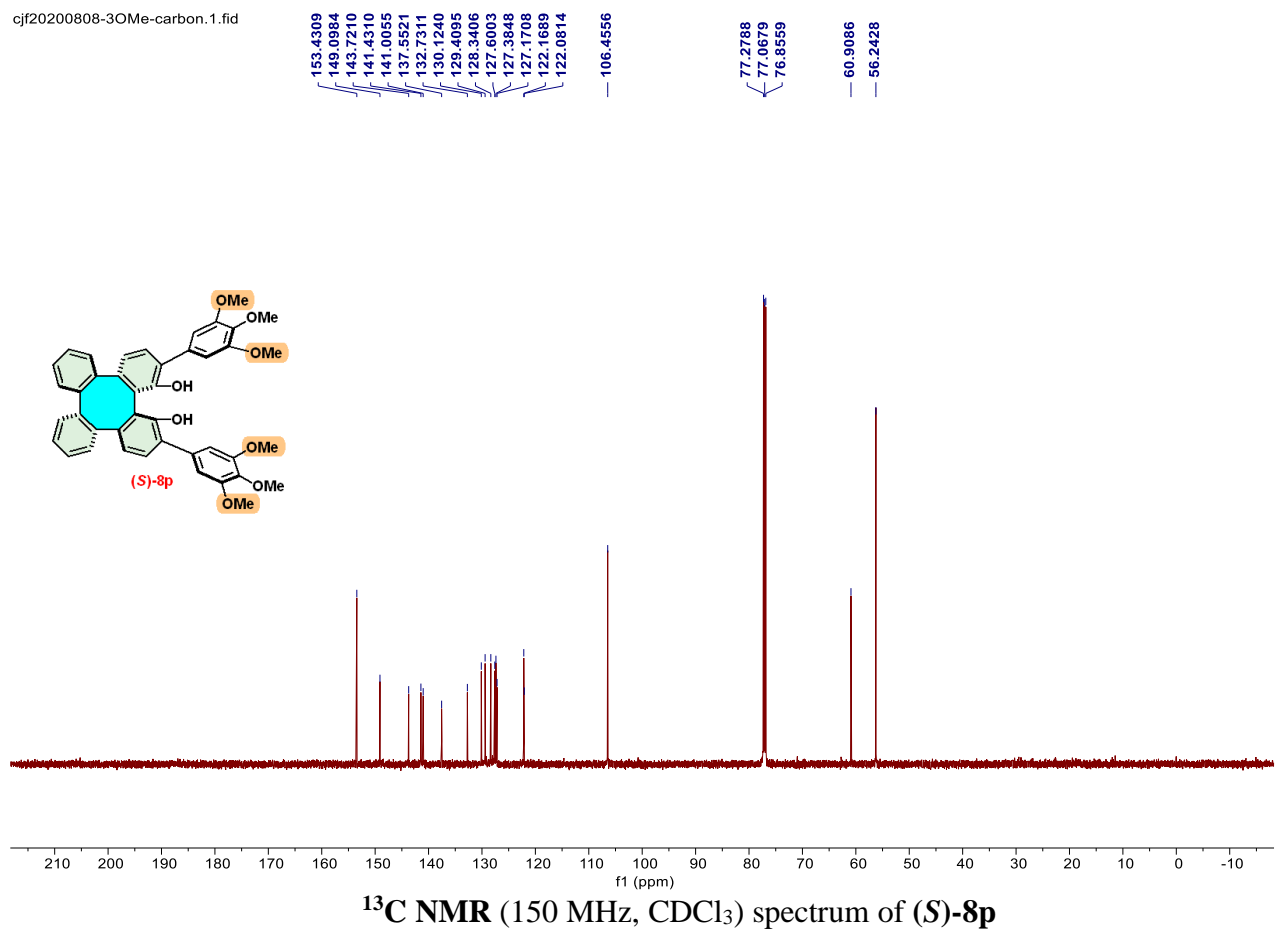
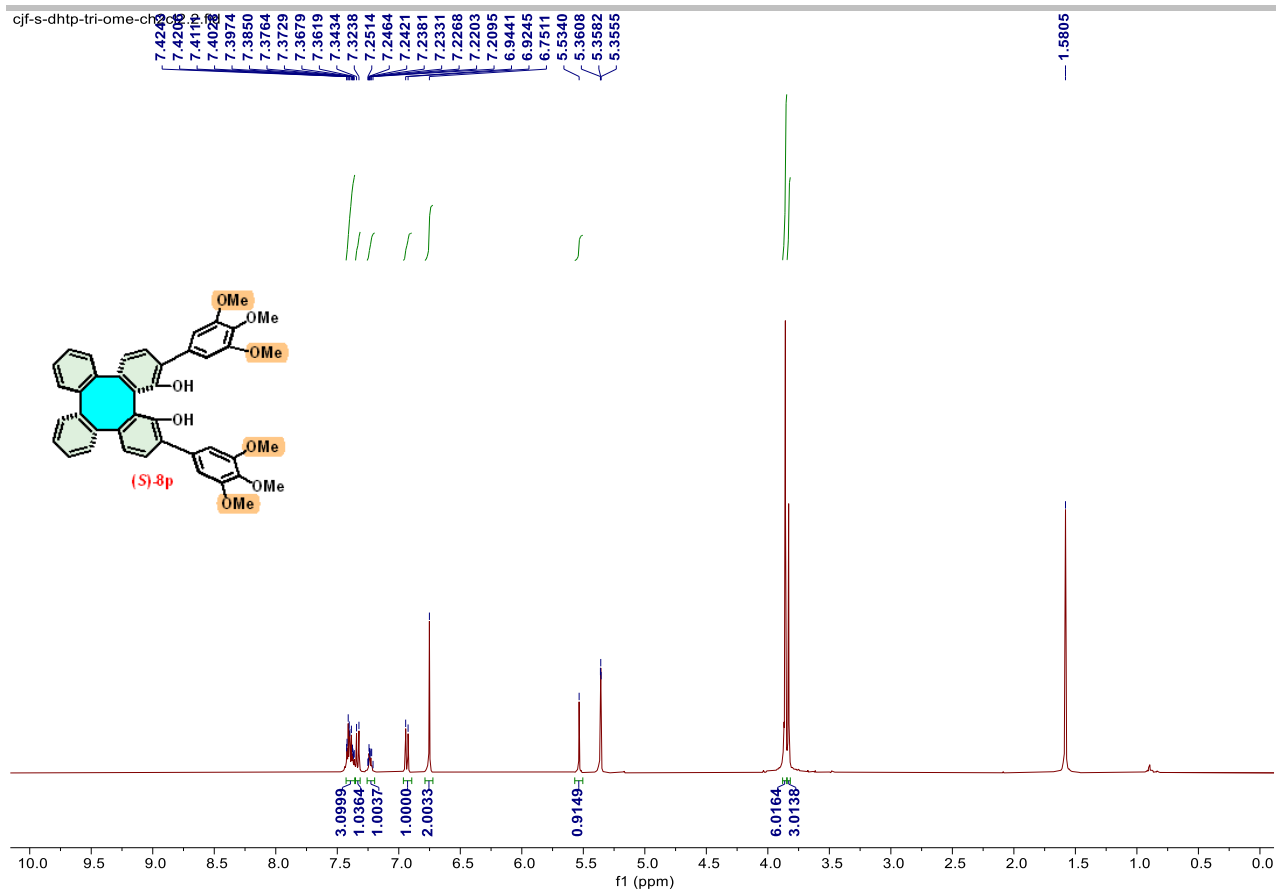
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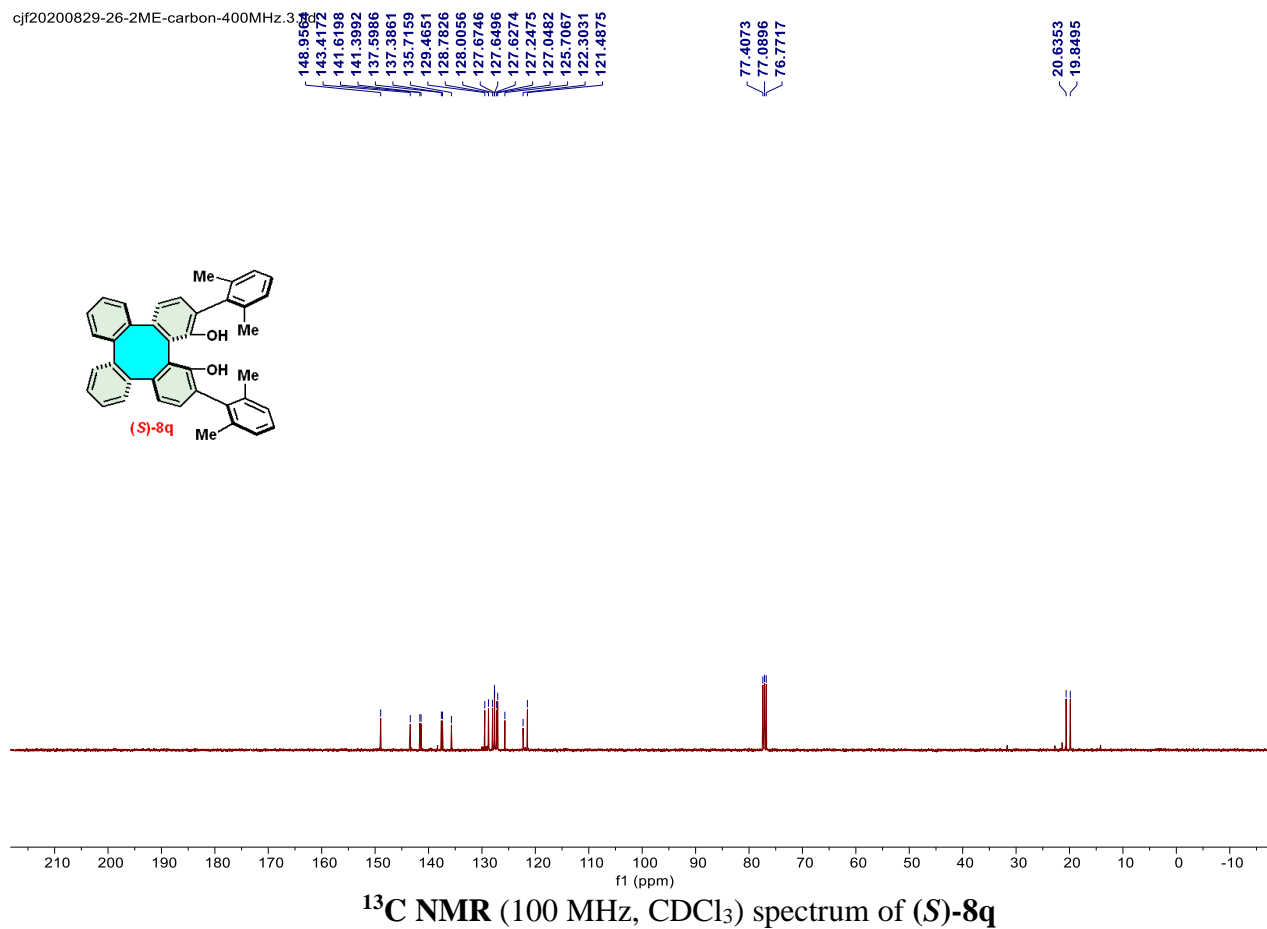
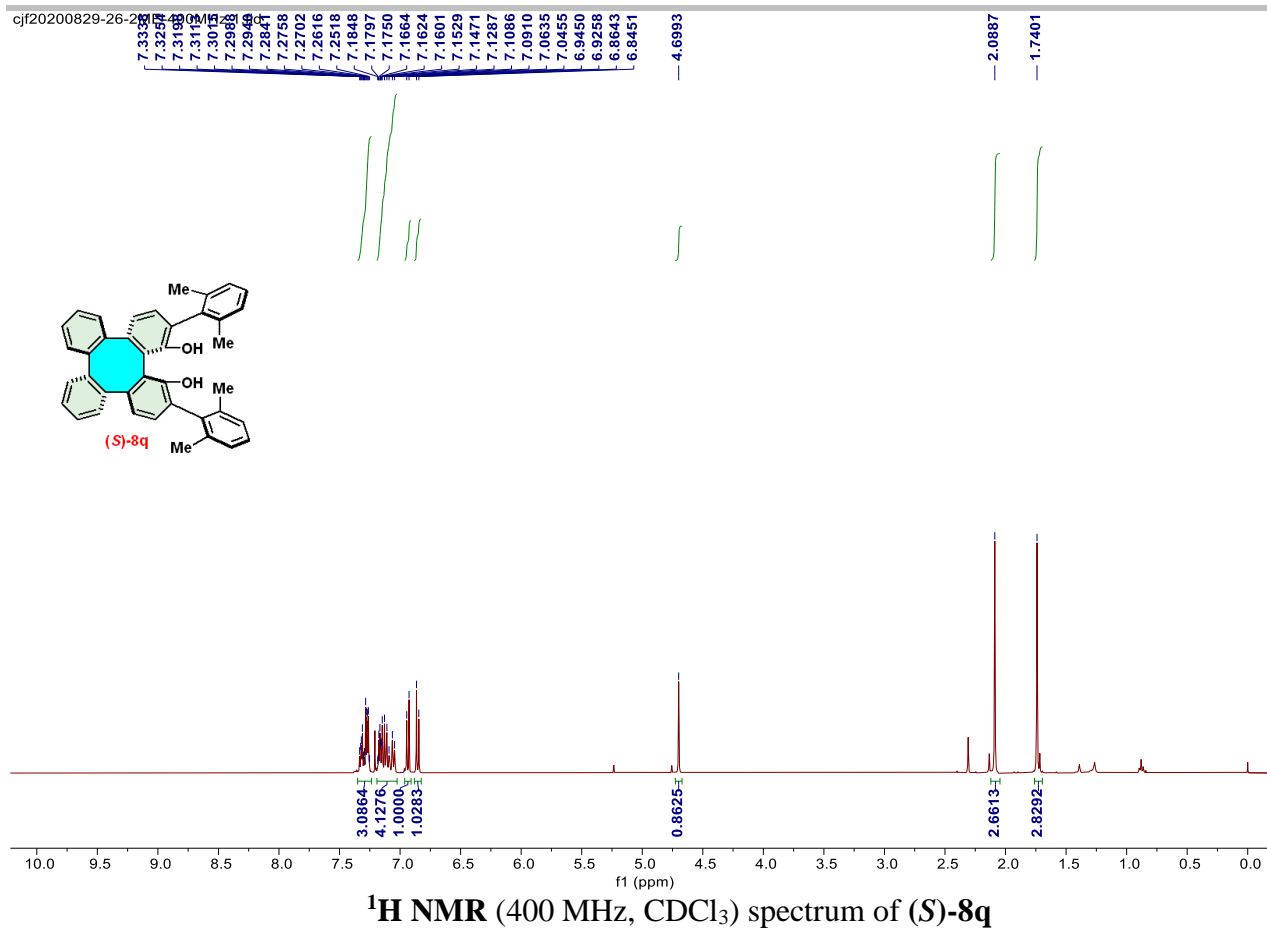
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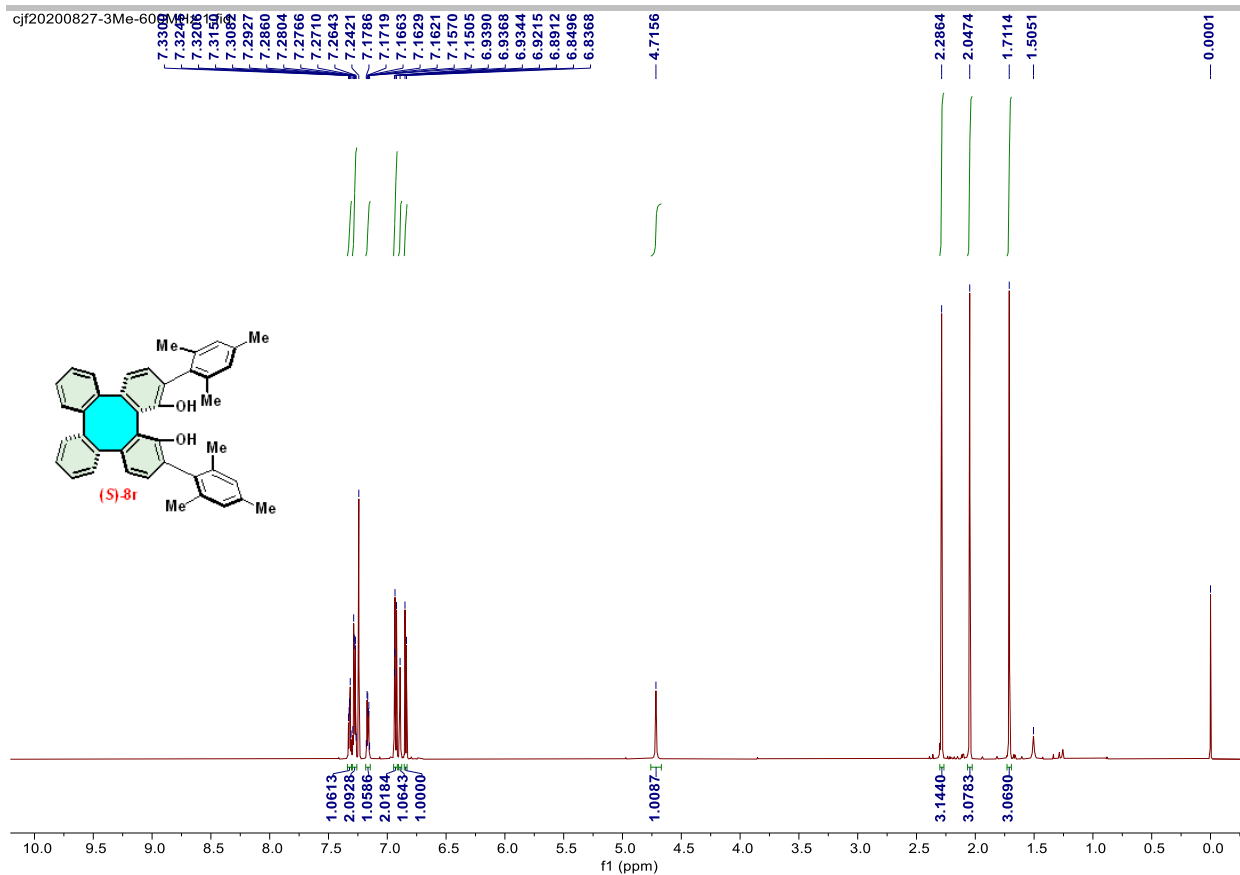
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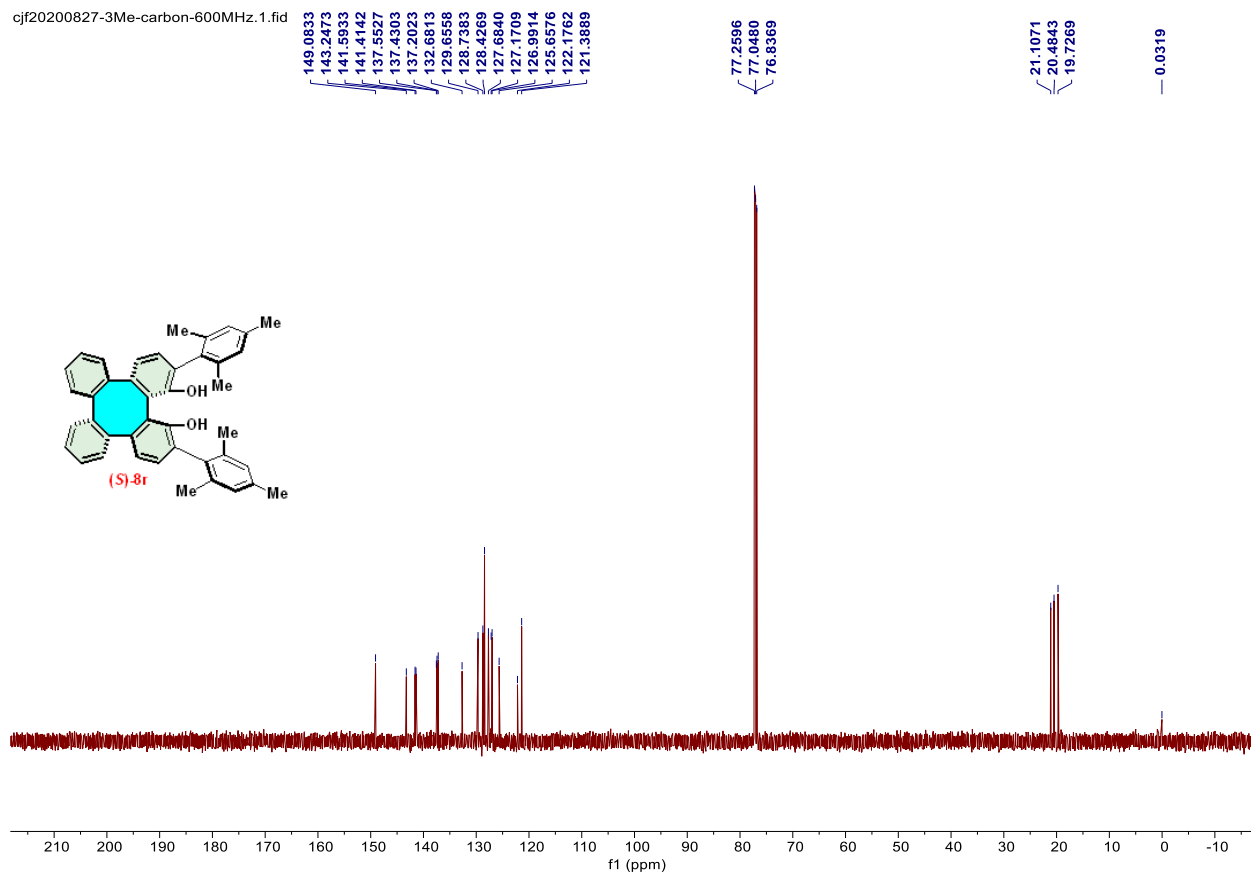
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SUPPORTING INFORMATION

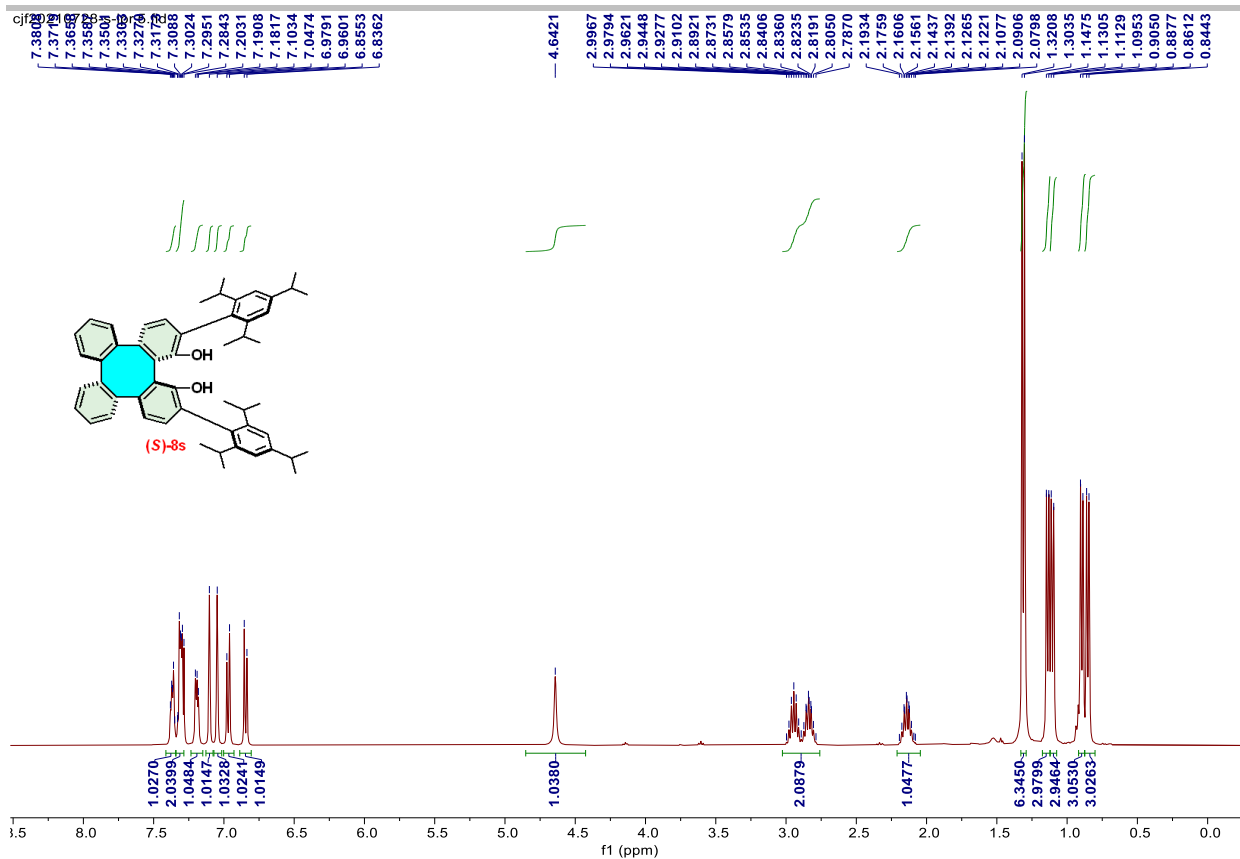


¹H NMR (600 MHz, CDCl₃) spectrum of (S)-8r



¹³C NMR (150 MHz, CDCl₃) spectrum of (S)-8r

SUPPORTING INFORMATION

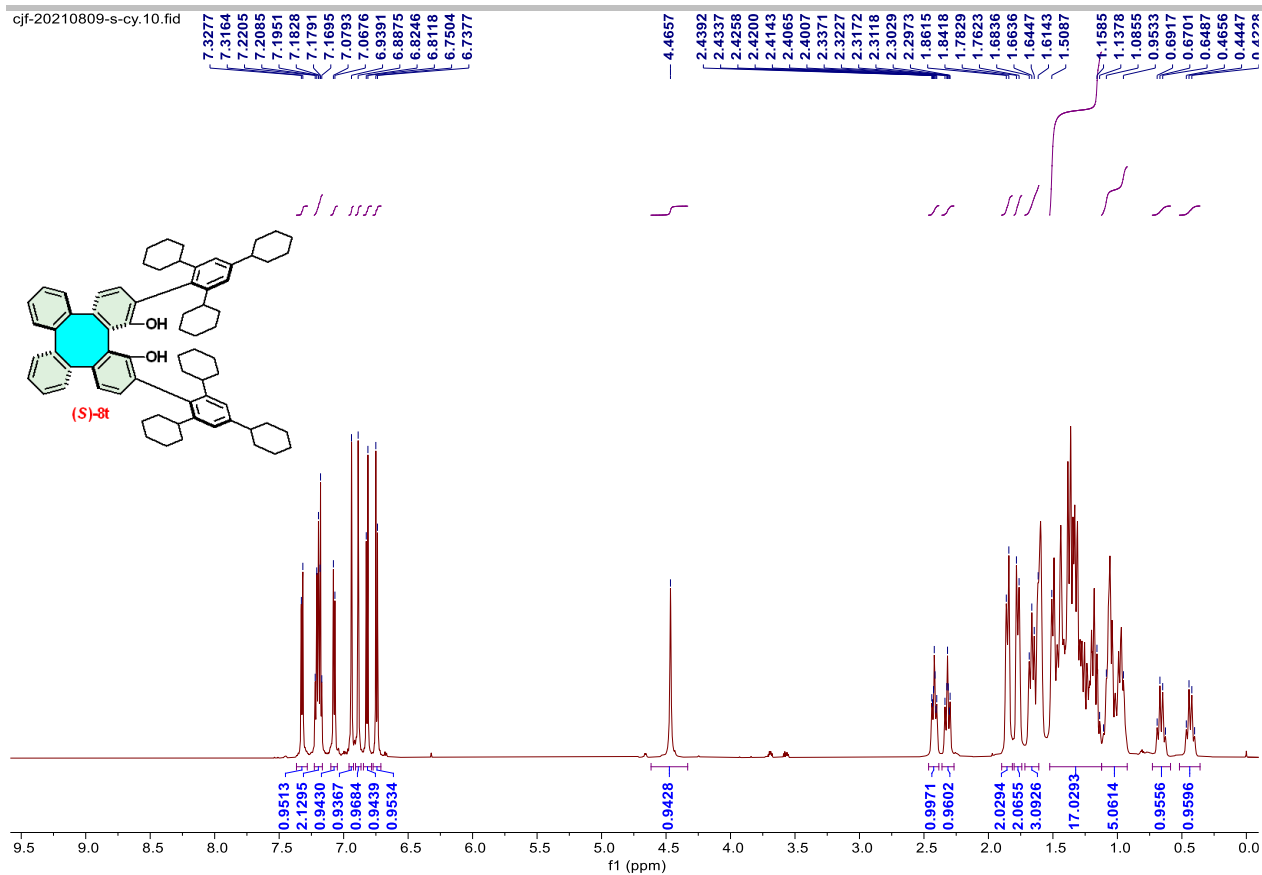


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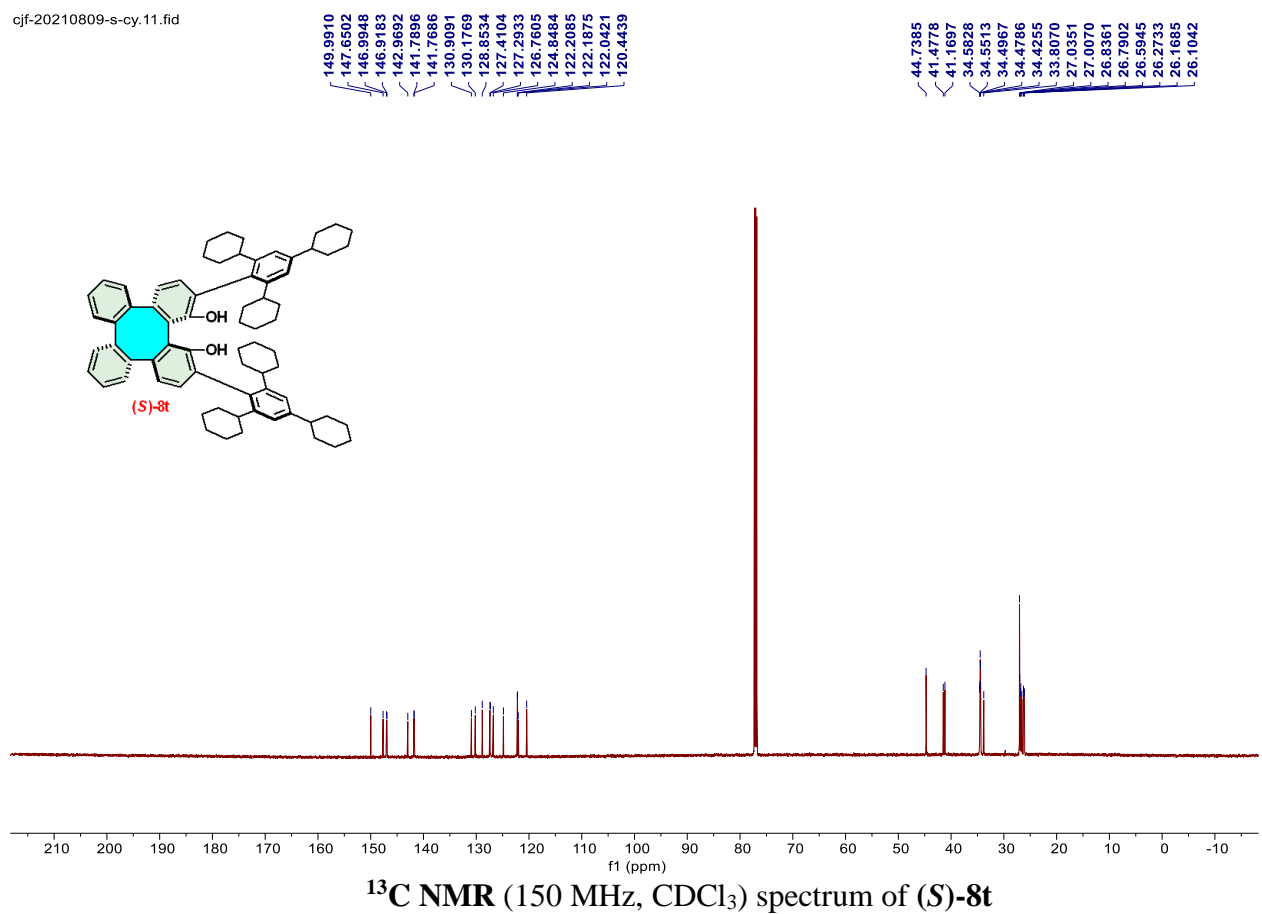


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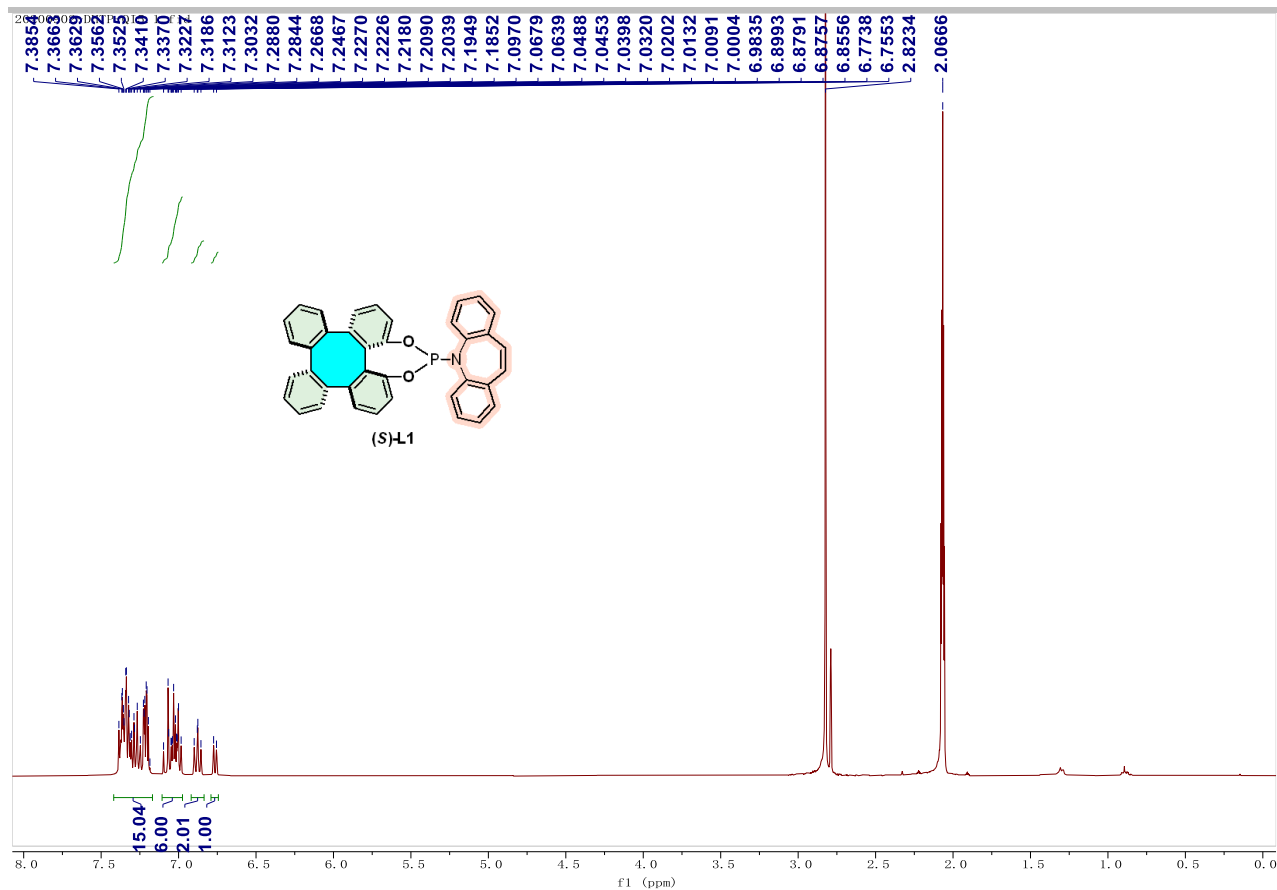
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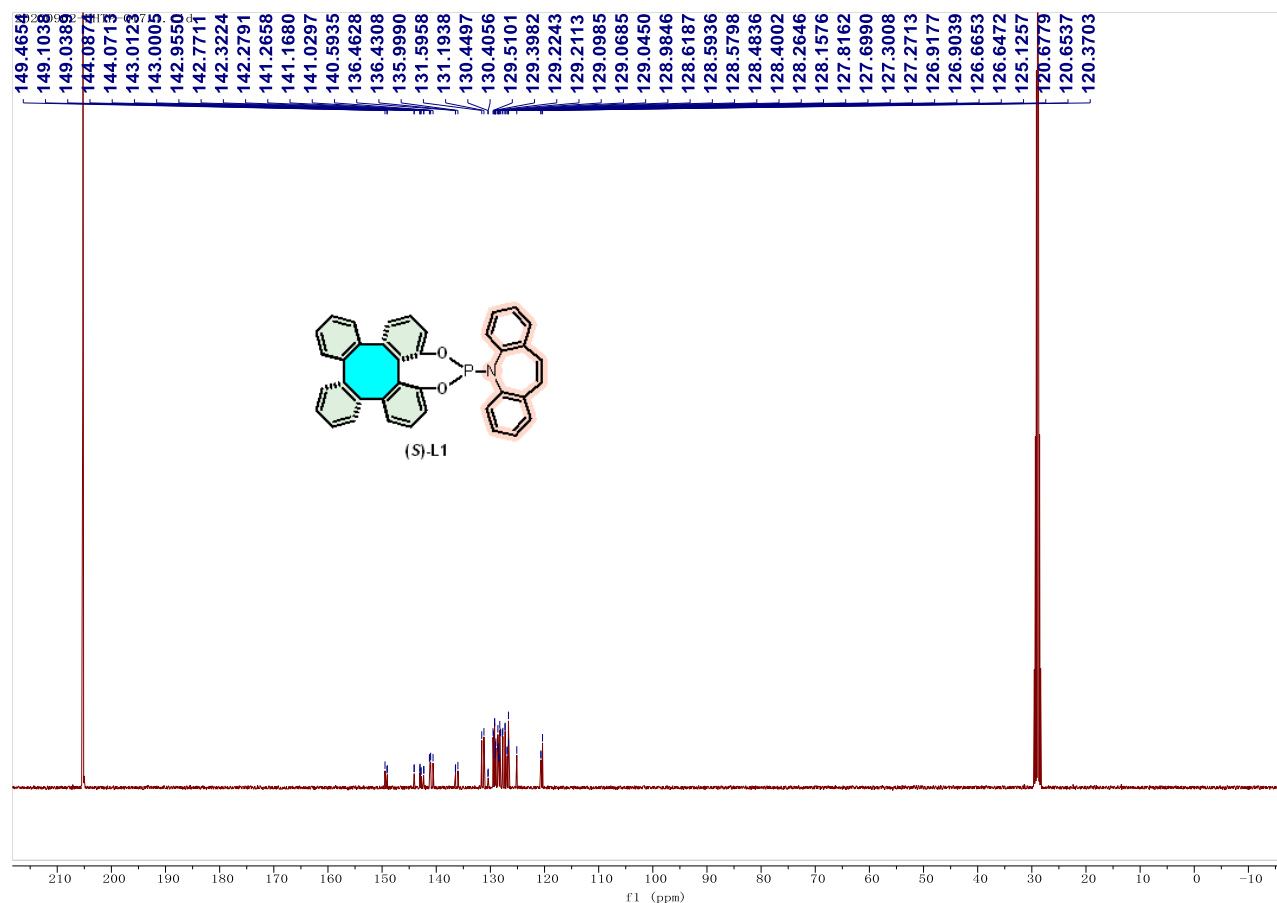
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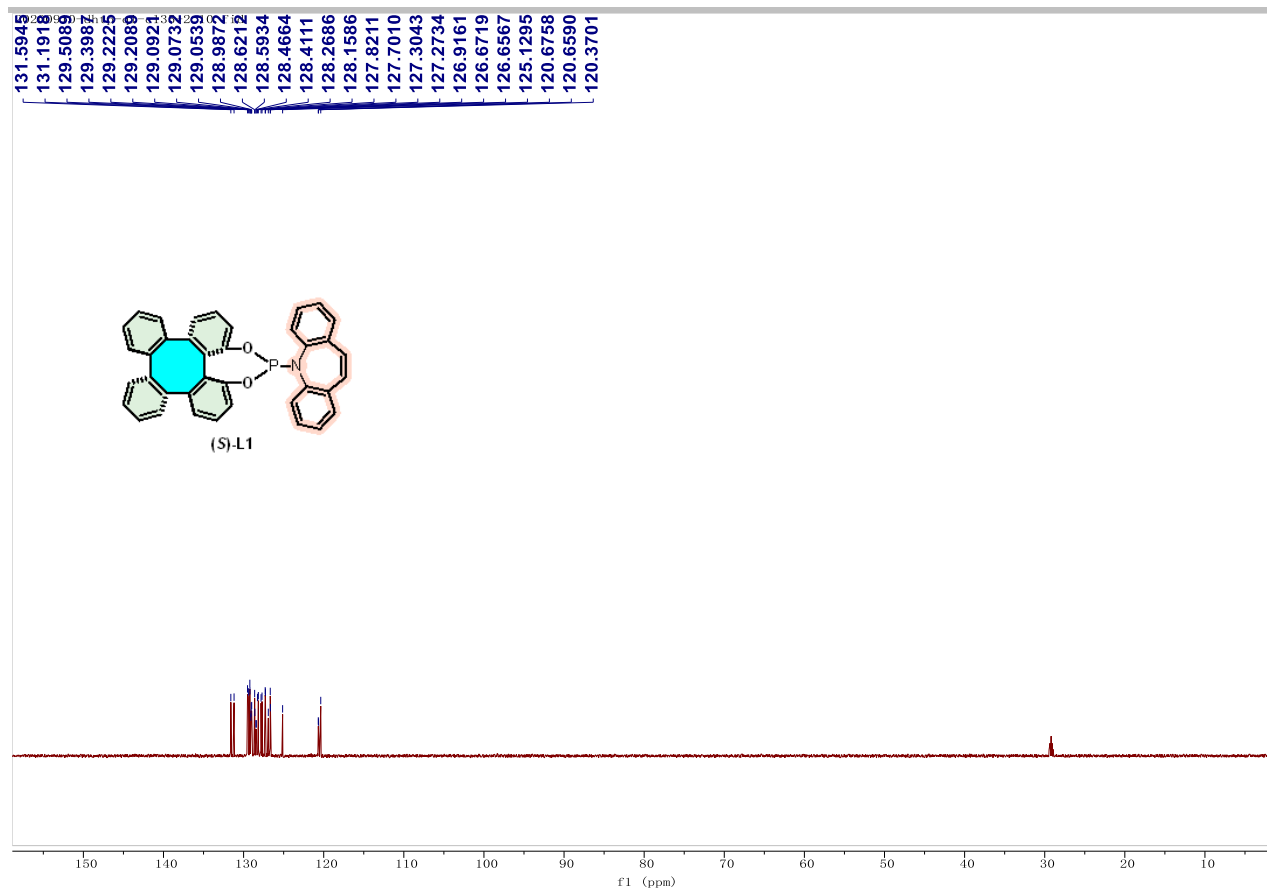


¹H NMR (400 MHz, Acetone-*d*₆) spectrum of (S)-L1

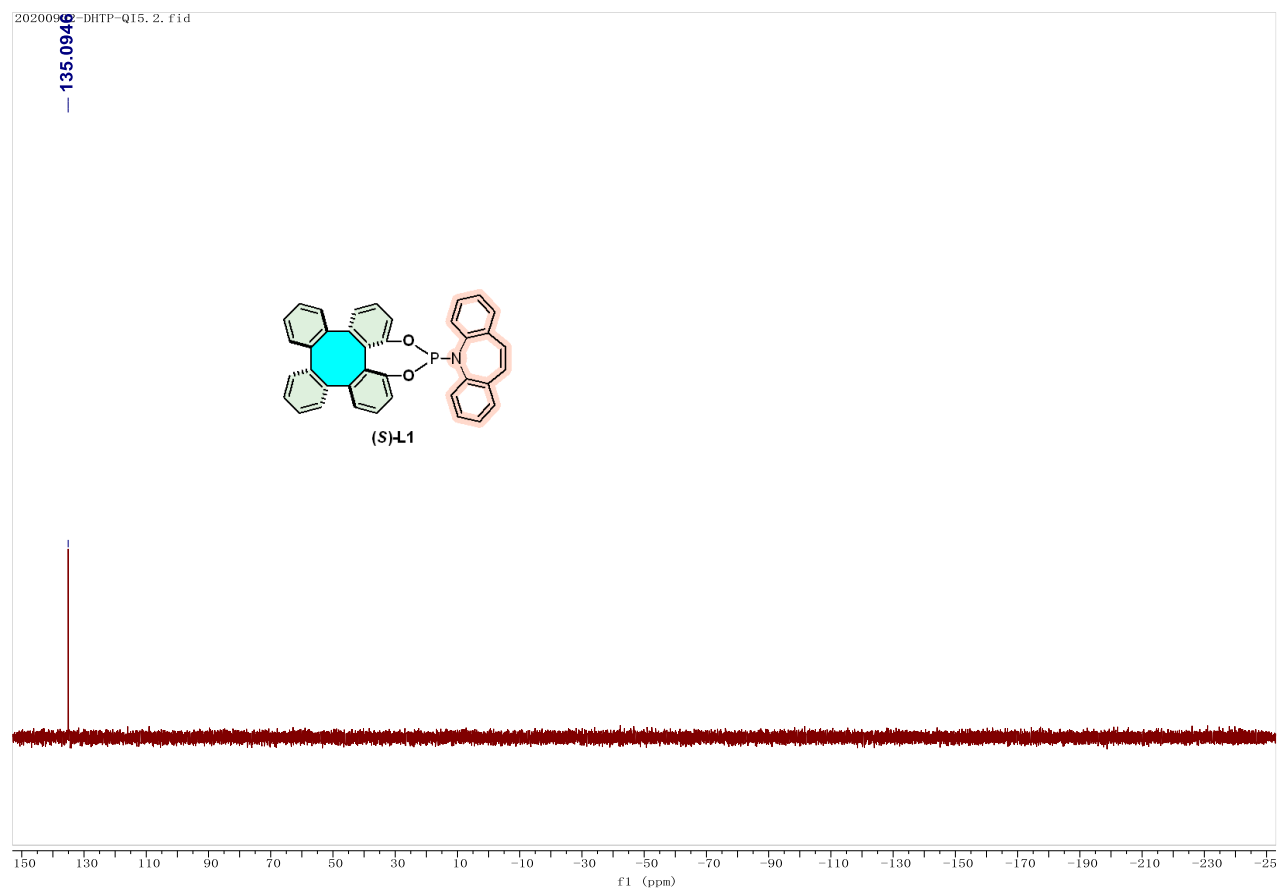


¹³C NMR (100 MHz, Acetone-*d*₆) spectrum of (S)-L1

SUPPORTING INFORMATION

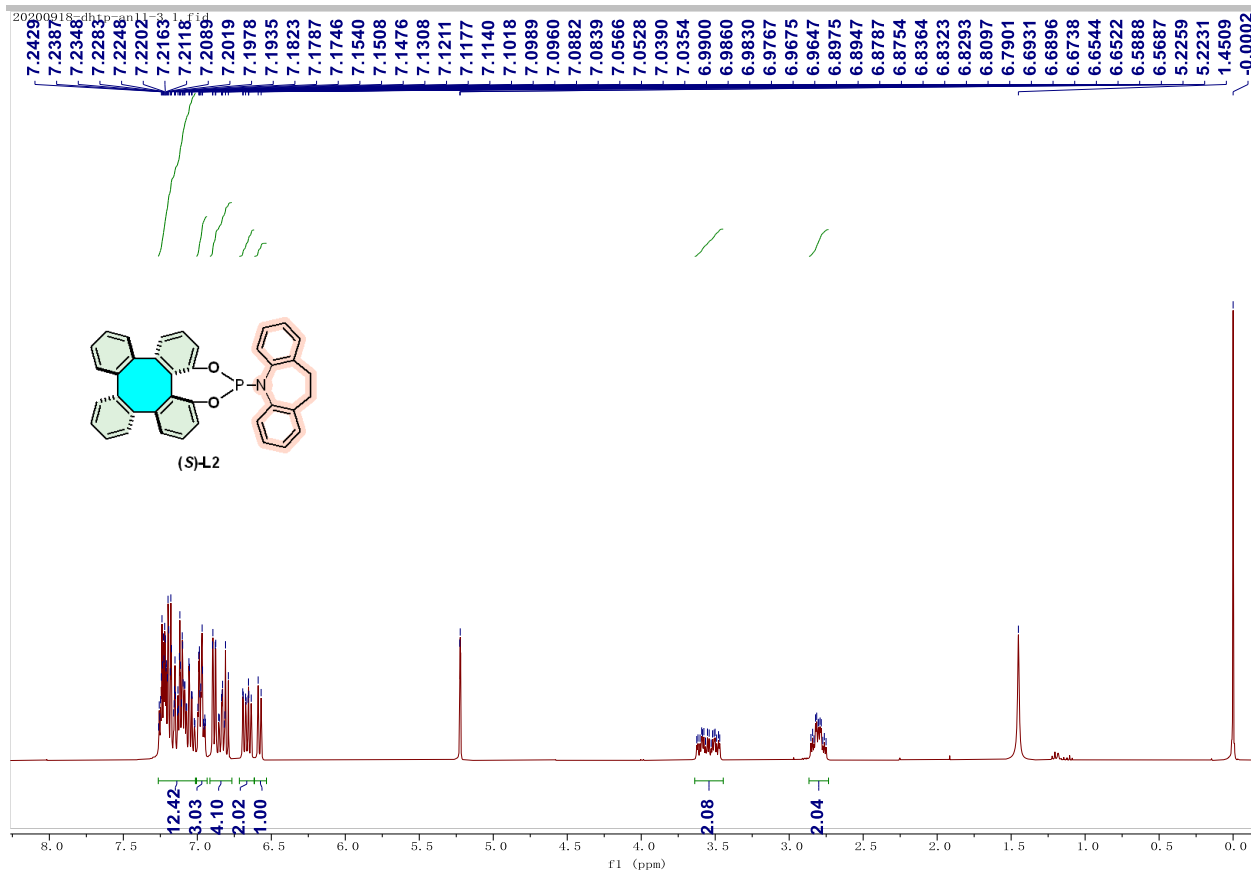


DEPT135 ^{13}C NMR (150 MHz, Acetone- d_6) spectrum of (S)-L1

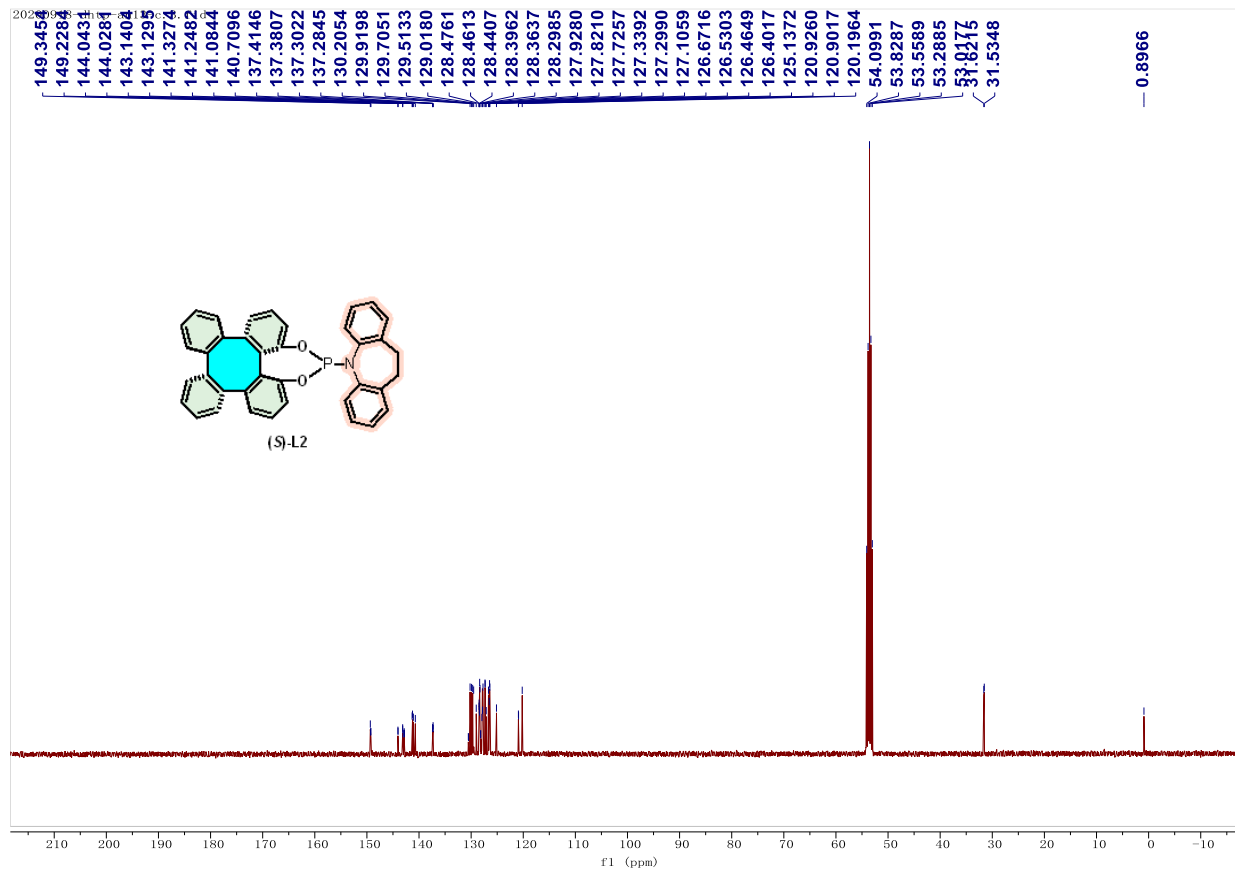


^{31}P NMR (162 MHz, Acetone- d_6) spectrum of (S)-L1

SUPPORTING INFORMATION



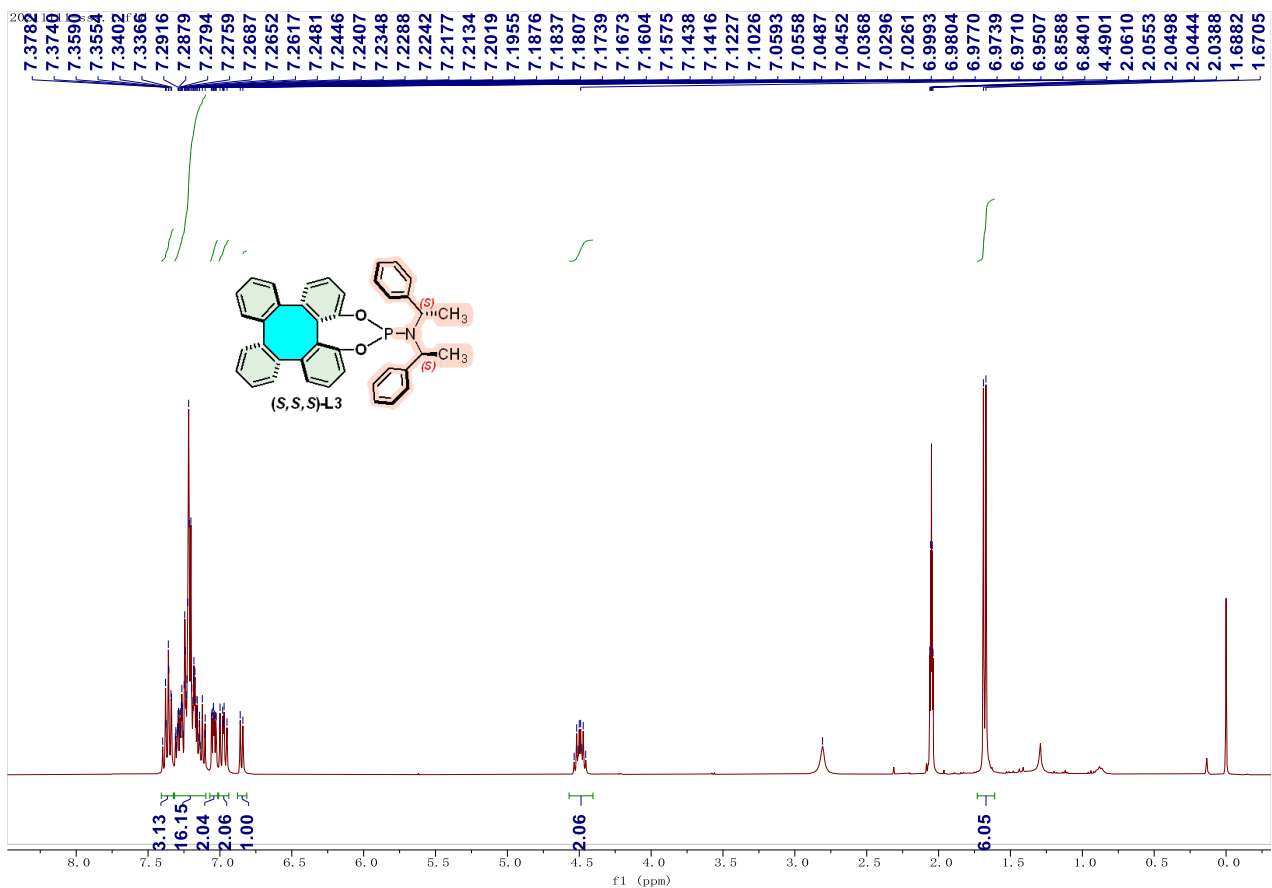
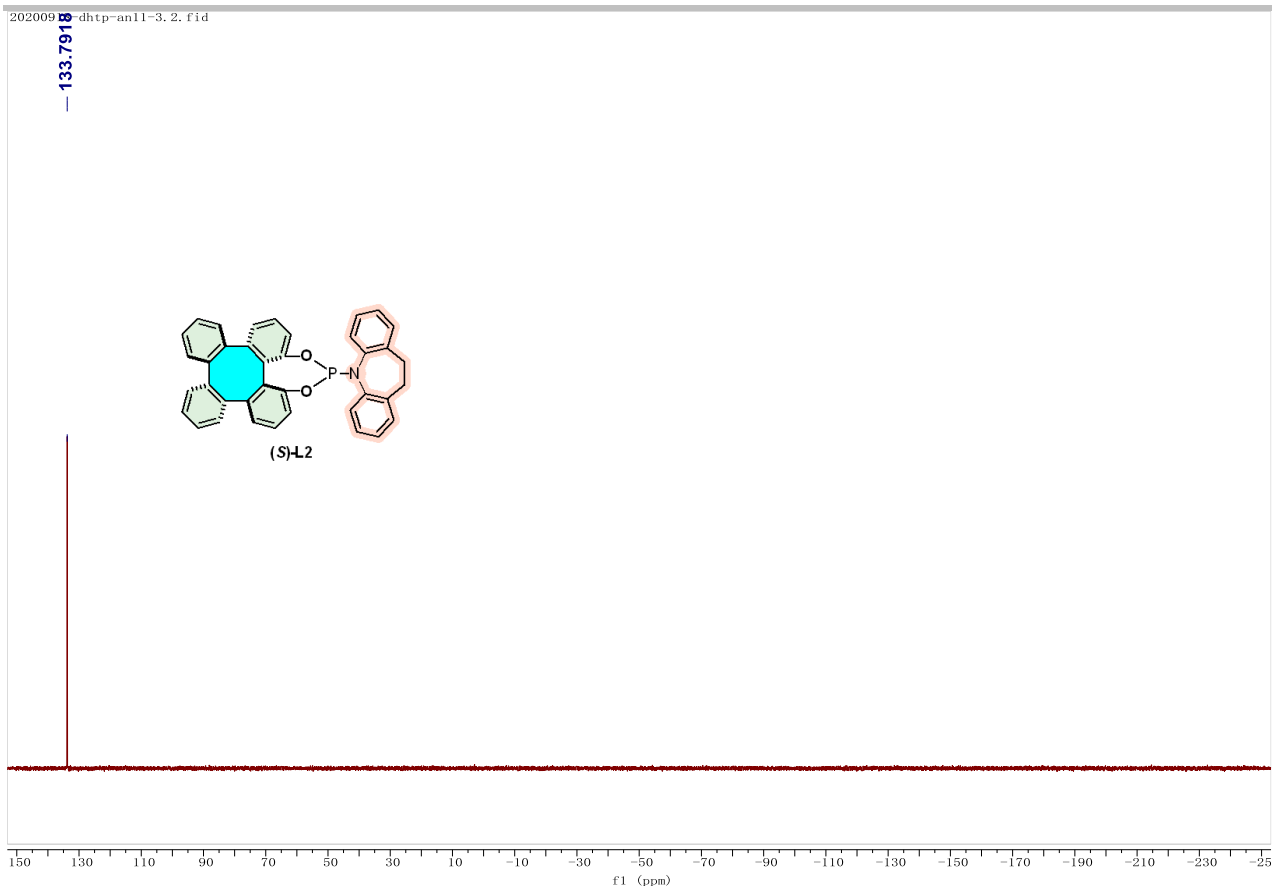
^1H NMR (400 MHz, CD_2Cl_2) spectrum of (S)-L2



^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of (S)-L2

SUPPORTING INFORMATION

20200918 dhtp-an11-3.2.fid



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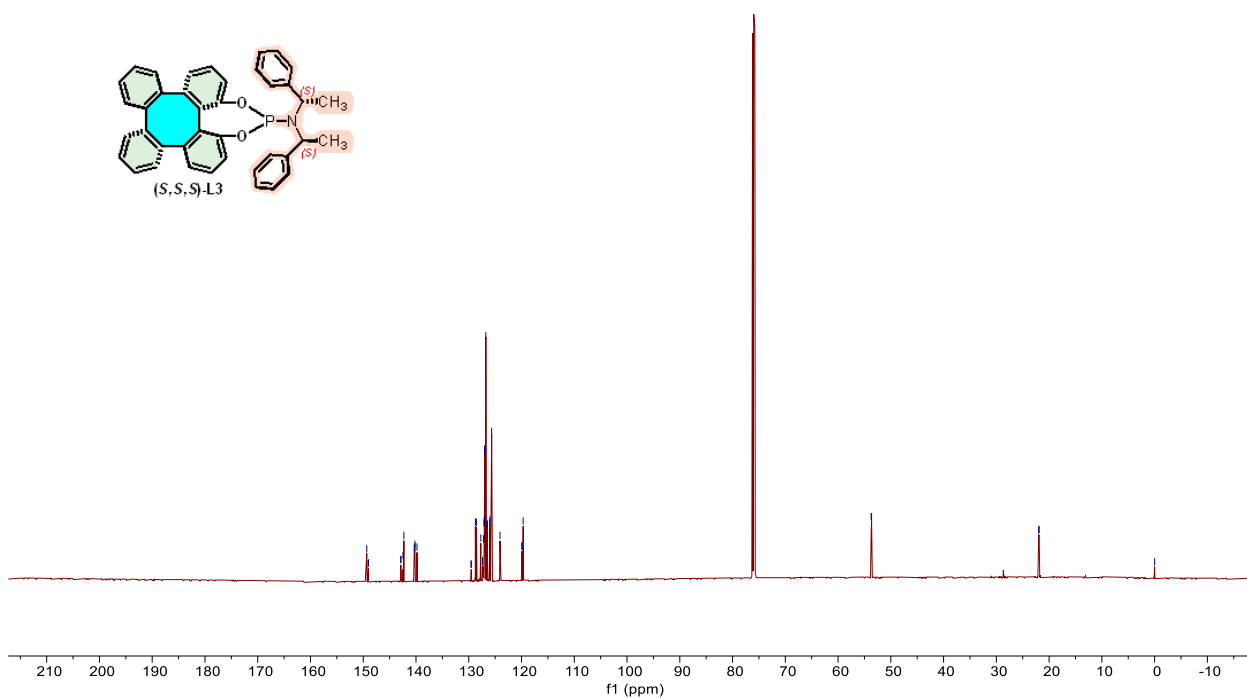
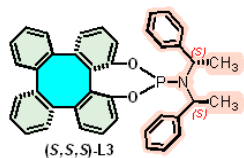
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128.7472
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127.7156
127.3946
127.3825
127.2216
127.1173
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125.9622
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119.9034
119.6937

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53.6470

21.9771
21.8974

-0.0021



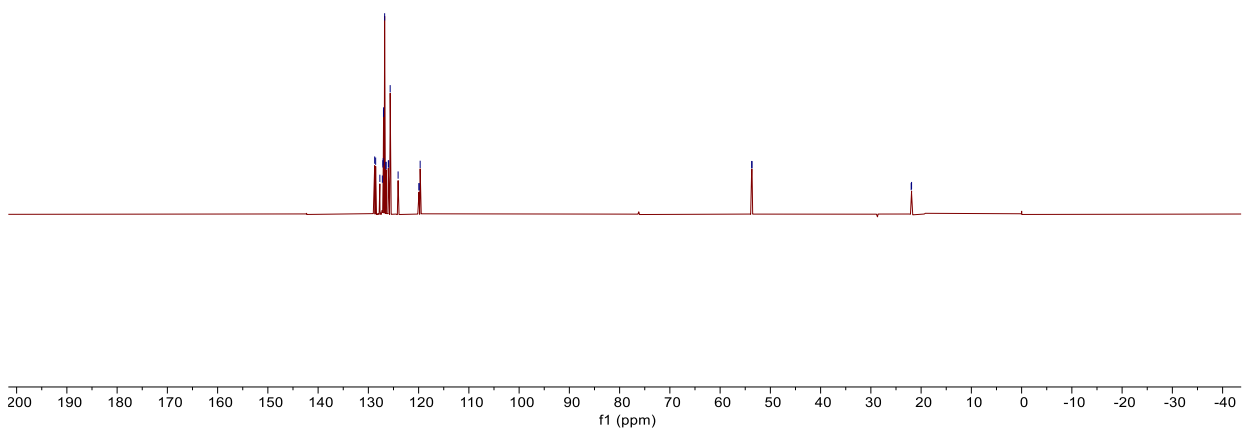
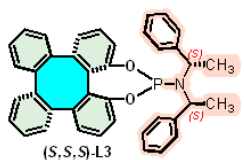
^{13}C NMR (150 MHz, CDCl_3) spectrum of (S,S,S)-L3

20211207-SSS.10.fid

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127.7143
127.2158
127.1162
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126.7617
126.5301
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53.7194
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21.9772
21.8975

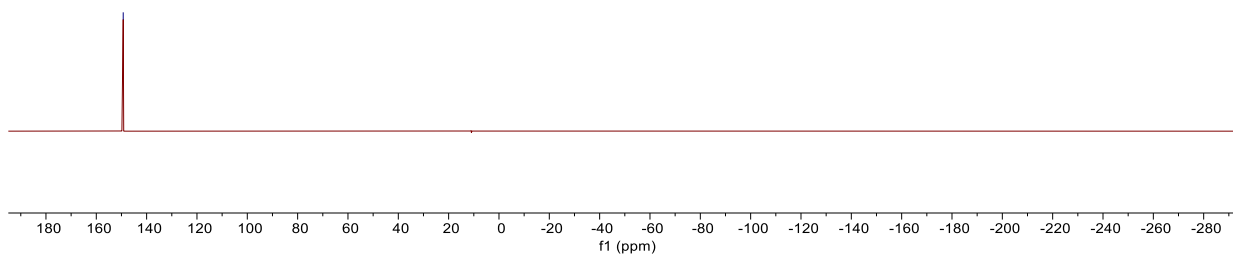
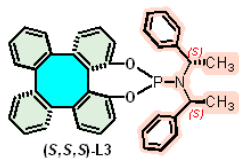


DEPT135 ^{13}C NMR (150 MHz, CDCl_3) spectrum of (S,S,S)-L3

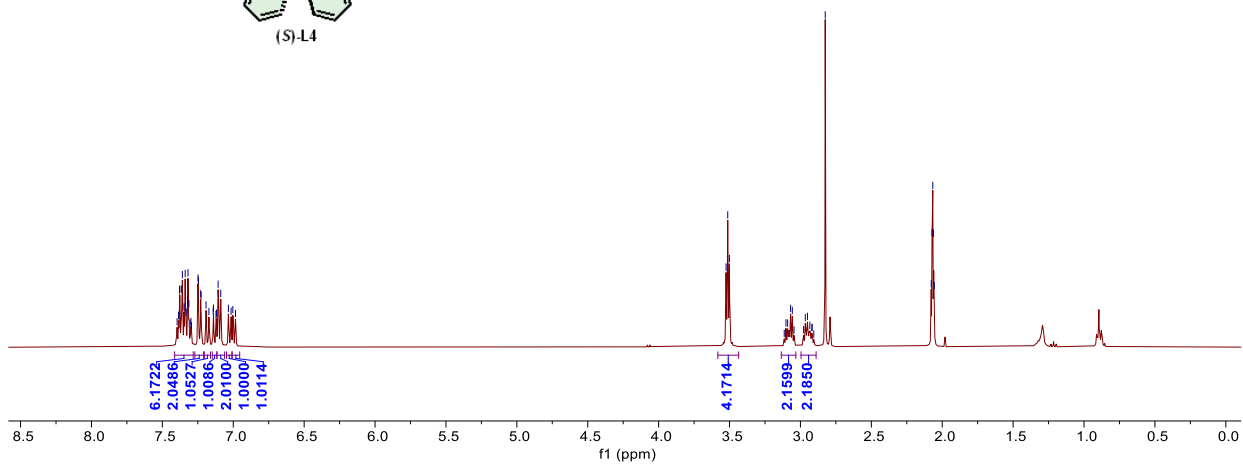
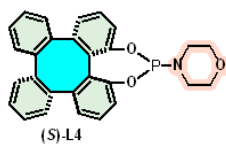
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20211205-SSS-15.fid

149.306



^{31}P NMR (243 MHz, CDCl_3) spectrum of (S,S,S)-L3

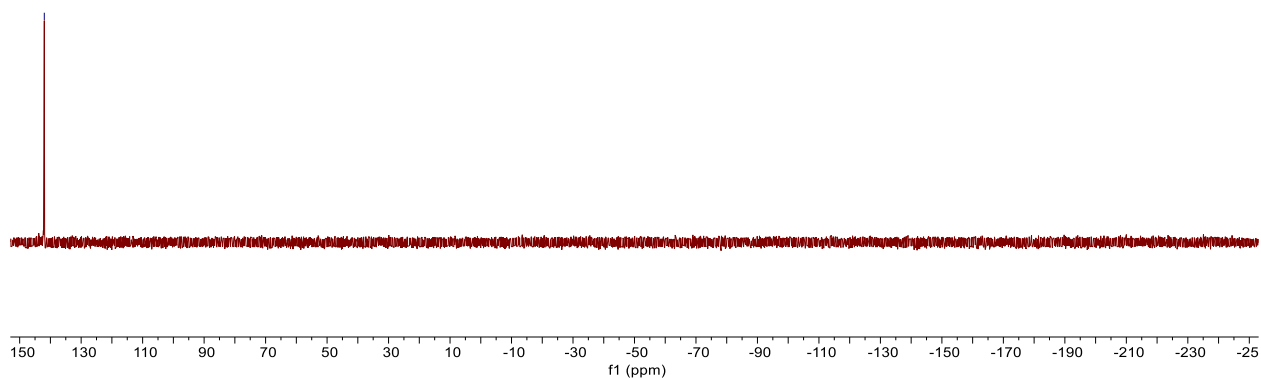
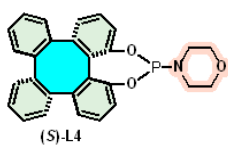


^1H NMR (400 MHz, $\text{Acetone-}d_6$) spectrum of (S)-L4

SUPPORTING INFORMATION

20200902-DHTP-MA9.2.fid

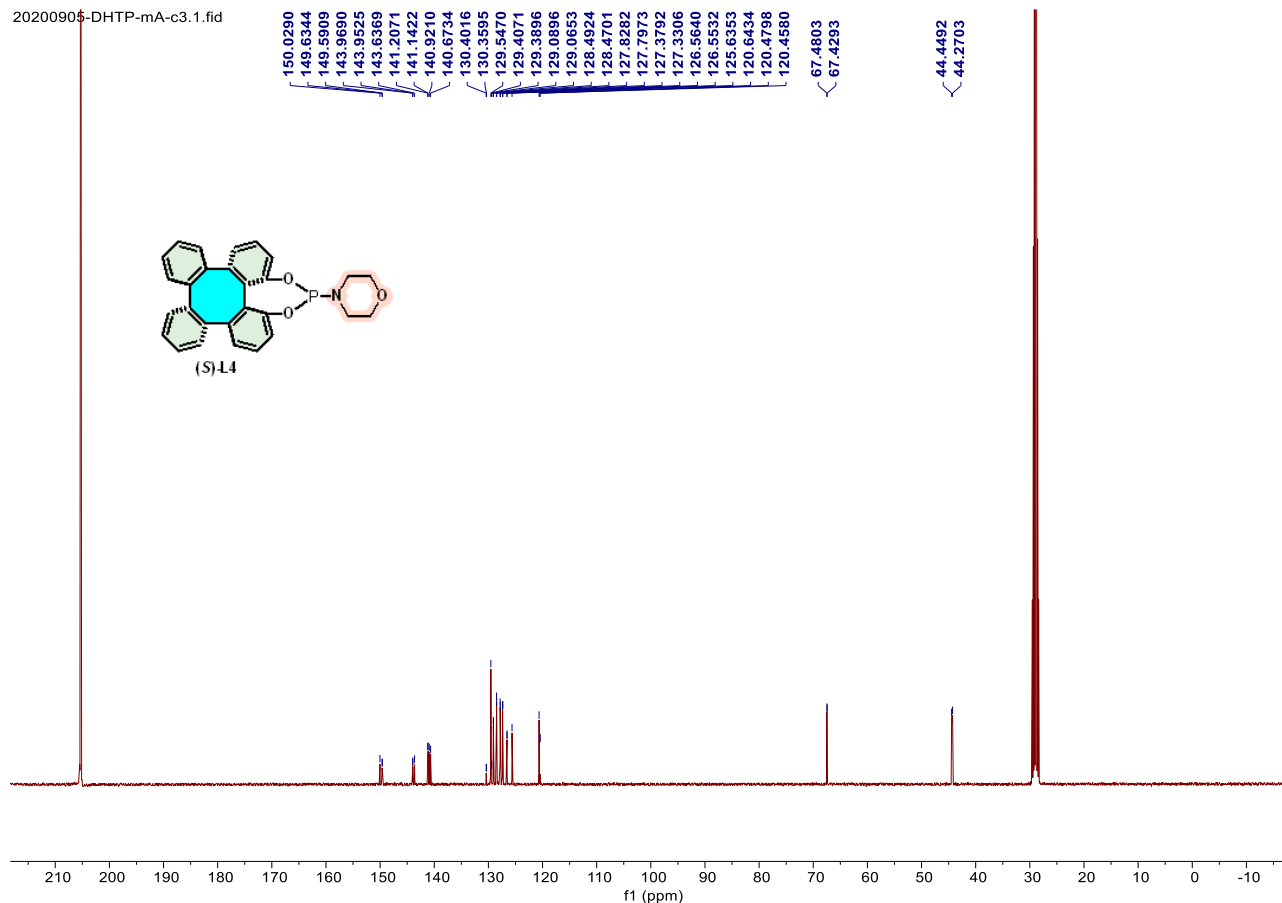
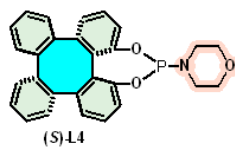
141.9863



^{31}P NMR (162 MHz, Acetone- d_6) spectrum of (S)-L4

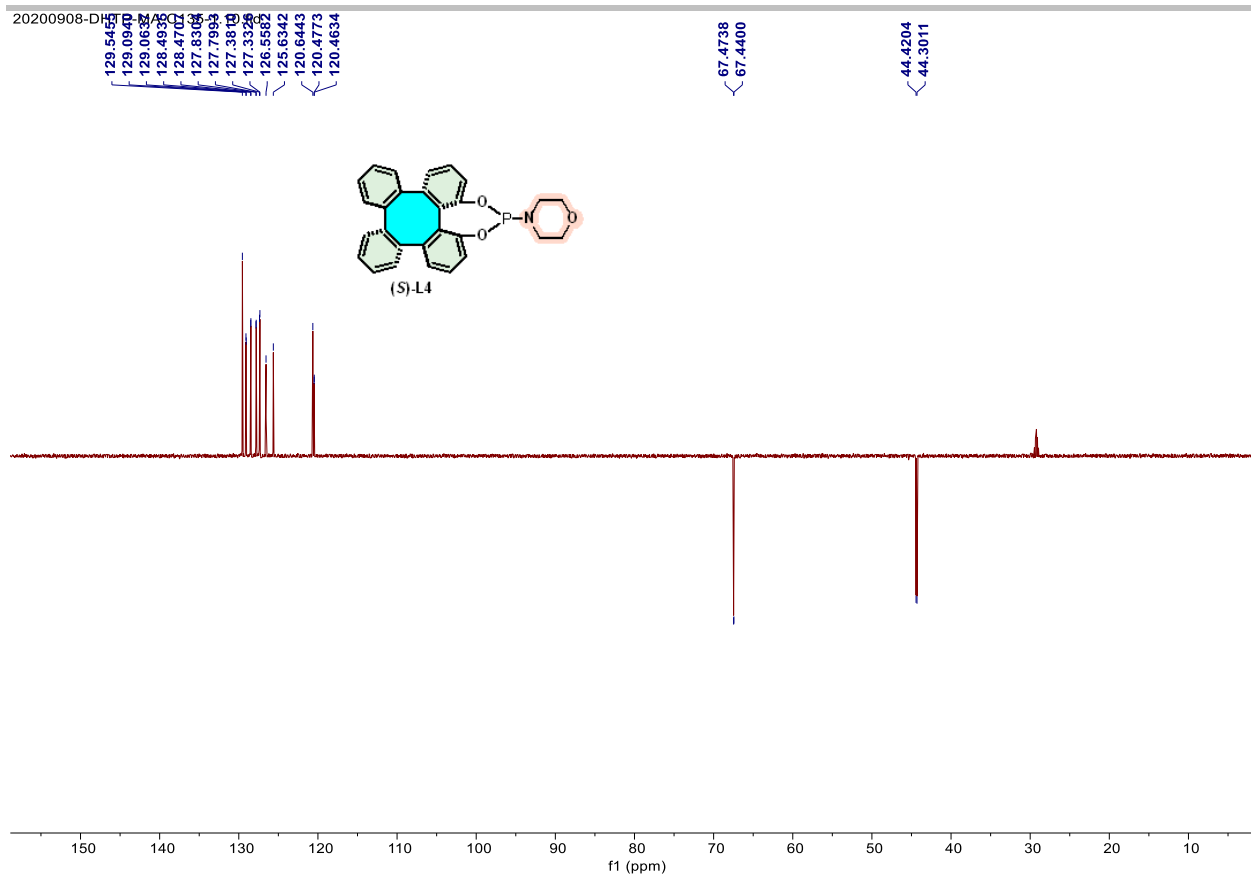
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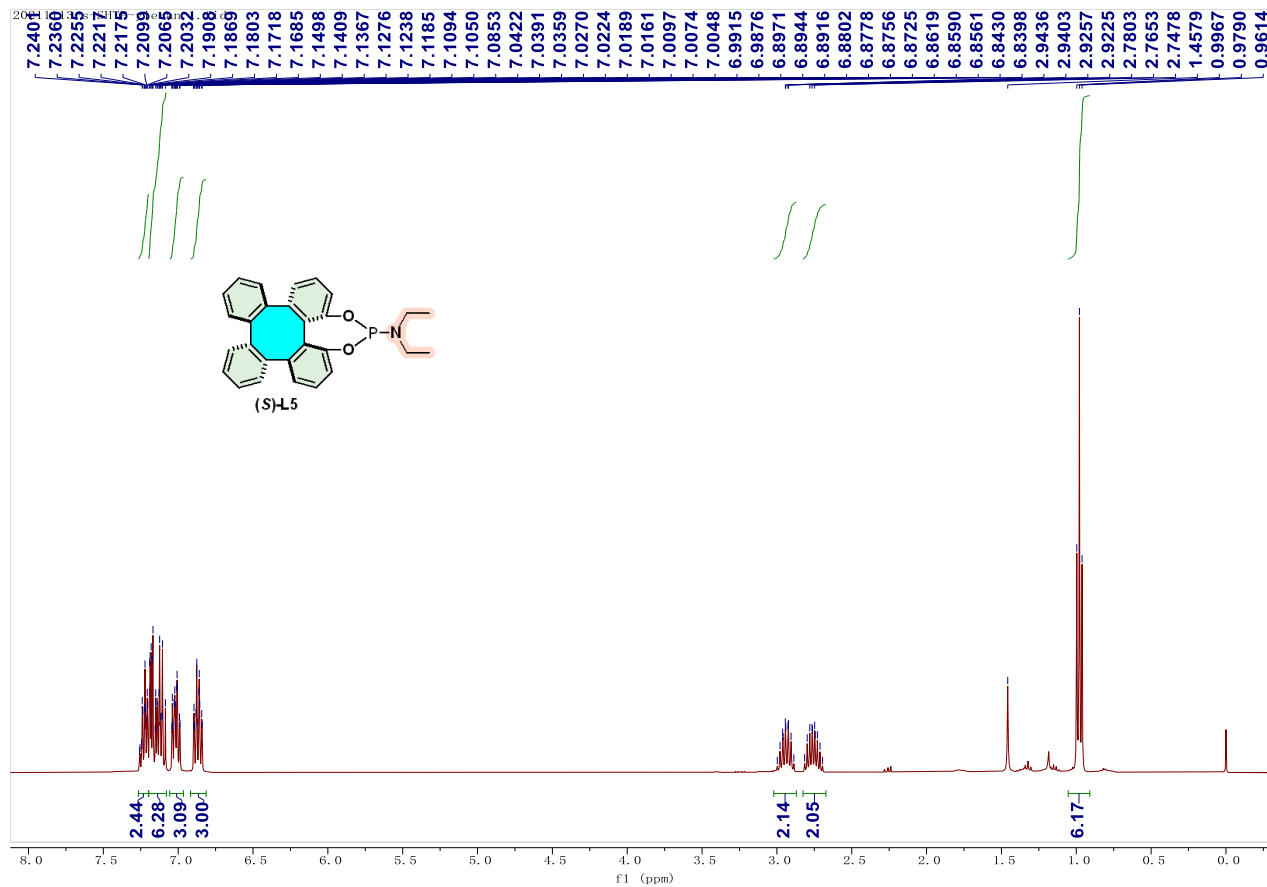


^{13}C NMR (150 MHz, Acetone- d_6) spectrum of (S)-L4

SUPPORTING INFORMATION

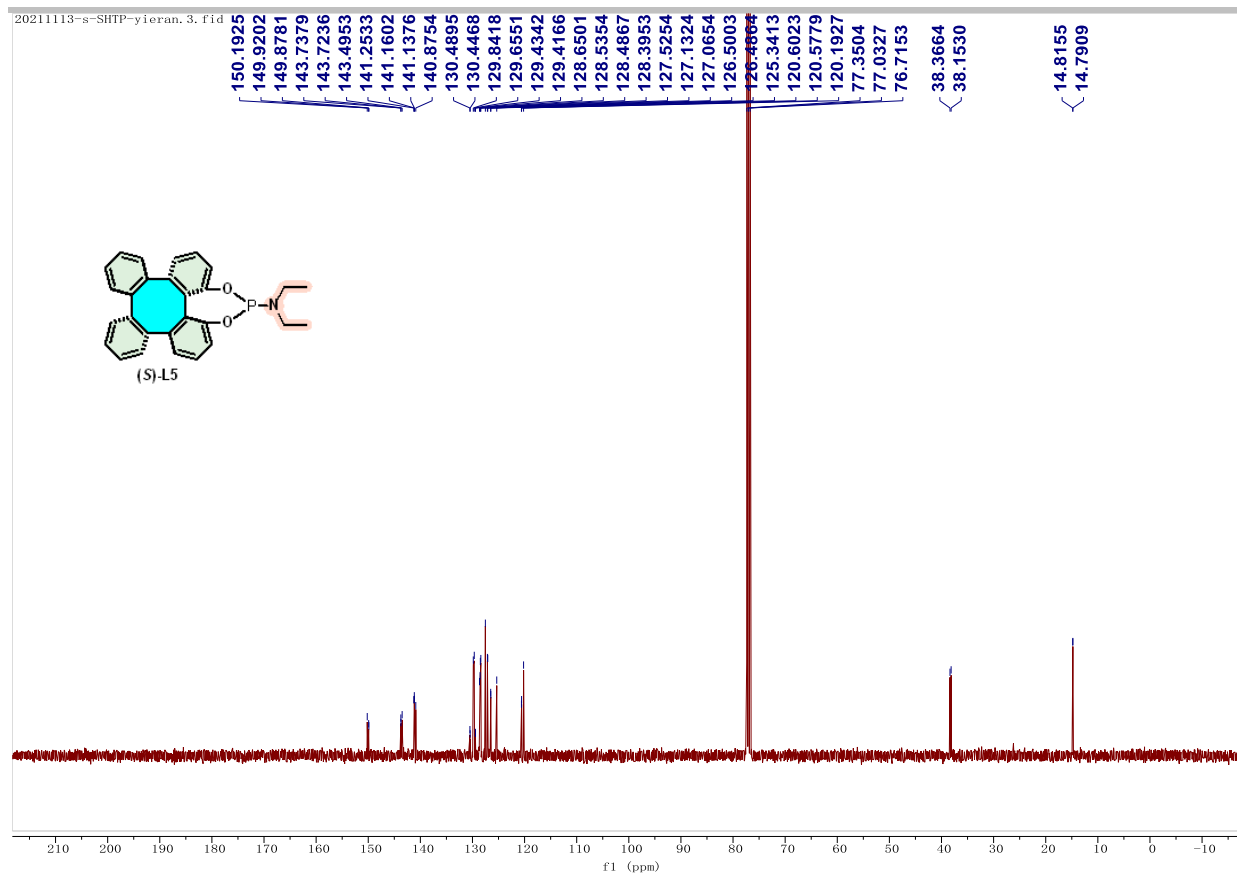


DEPT135 ^{13}C NMR (150 MHz, Acetone- d_6) spectrum of (S)-L4

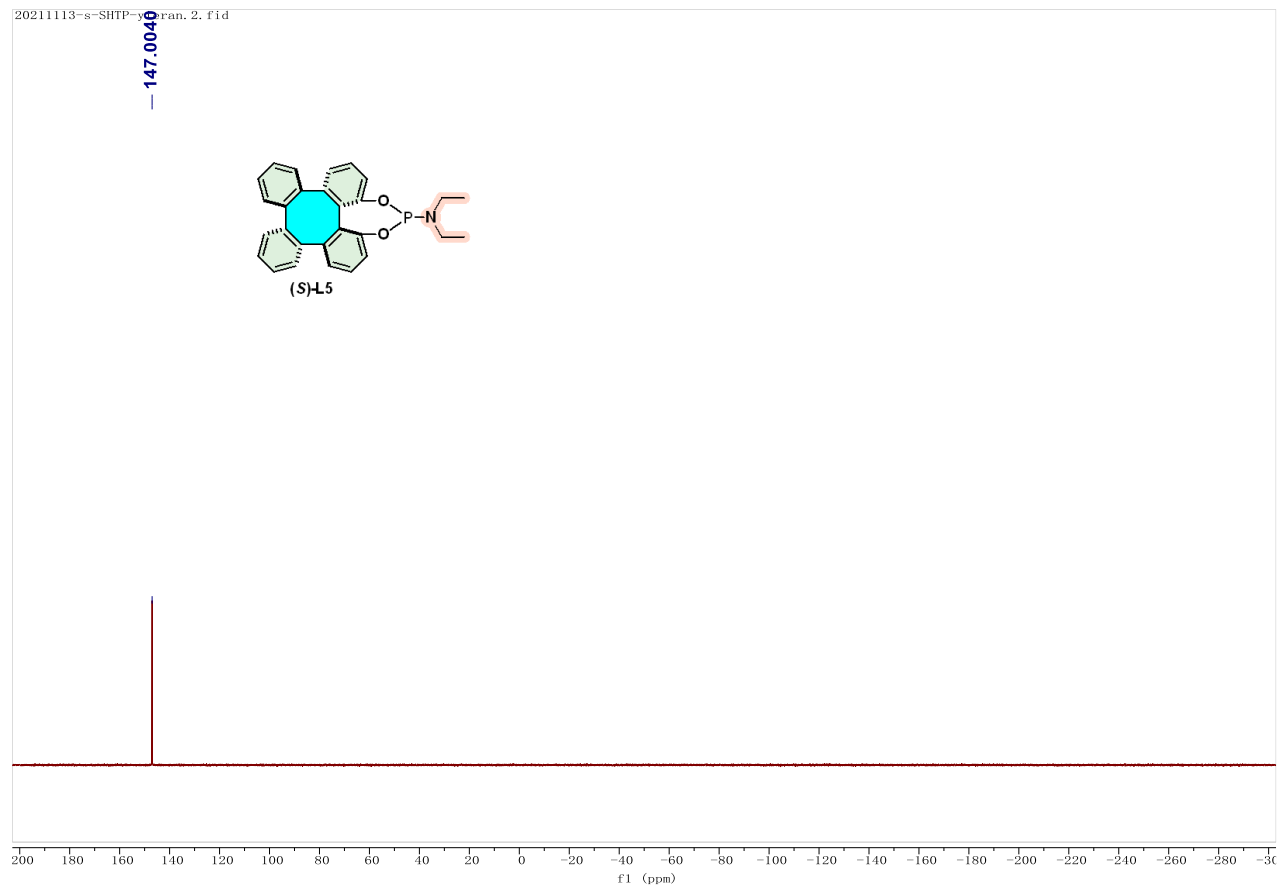


^1H NMR (400 MHz, CDCl_3) spectrum of (S)-L5

SUPPORTING INFORMATION

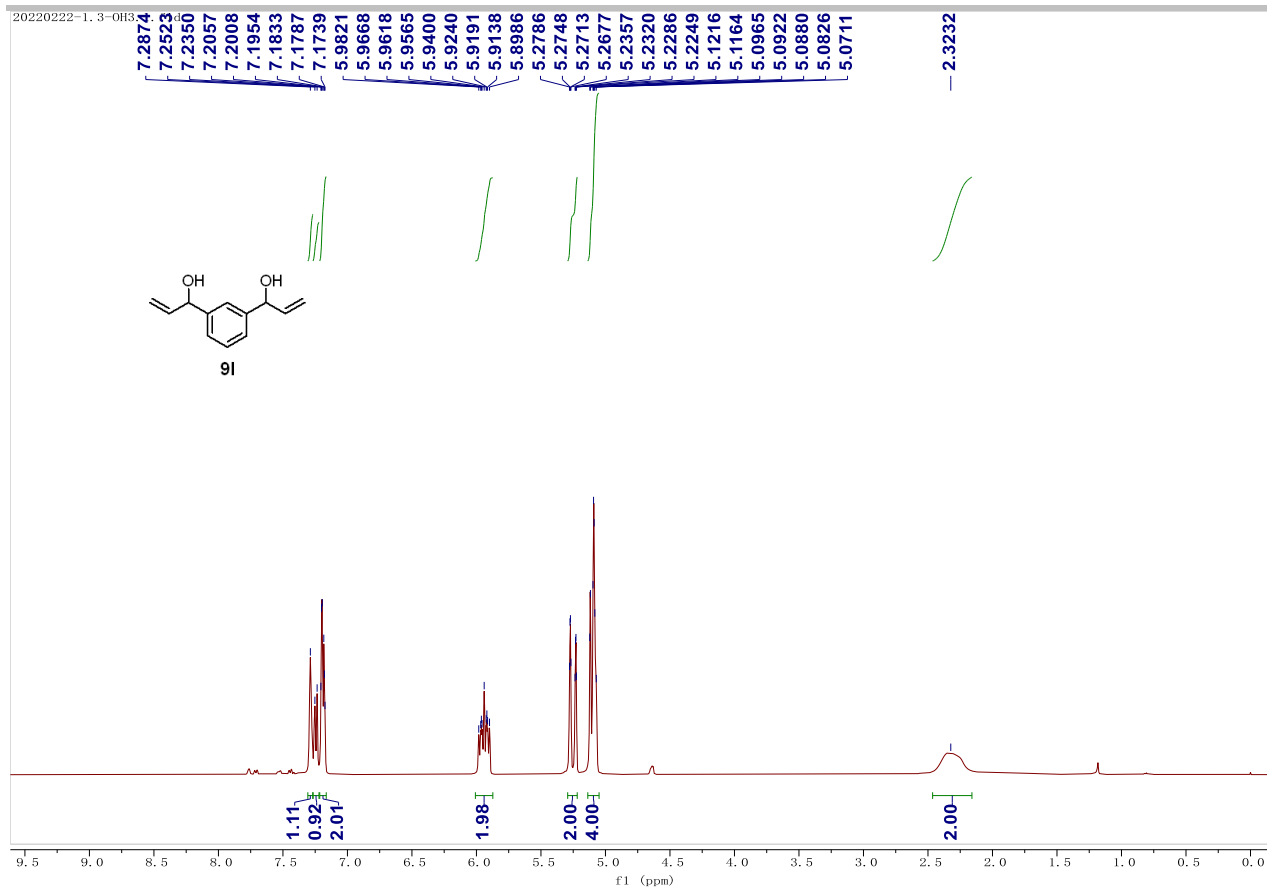


^{13}C NMR (100 MHz, CDCl_3) spectrum of (S)-L5

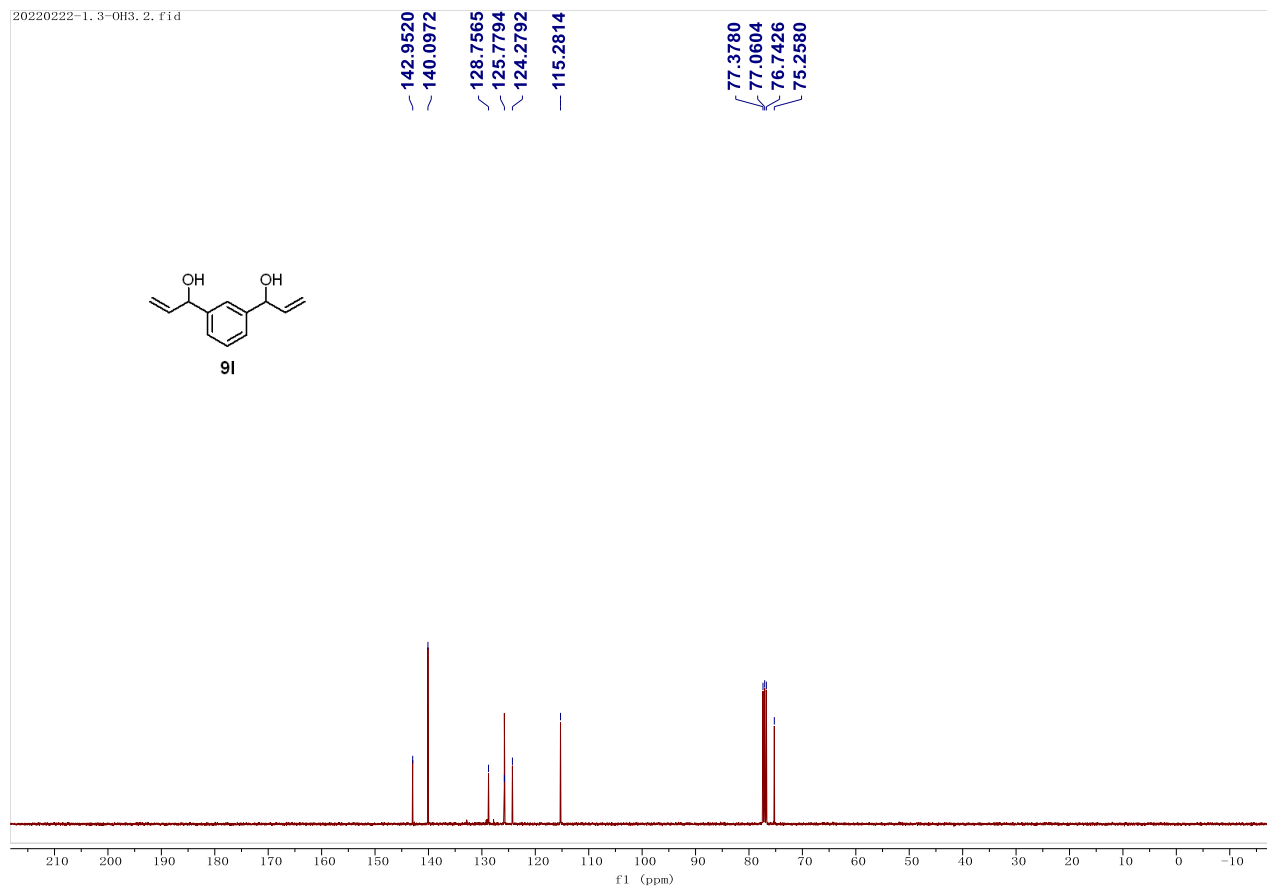


^{31}P NMR (162 MHz, CDCl_3) spectrum of (S)-L5

SUPPORTING INFORMATION

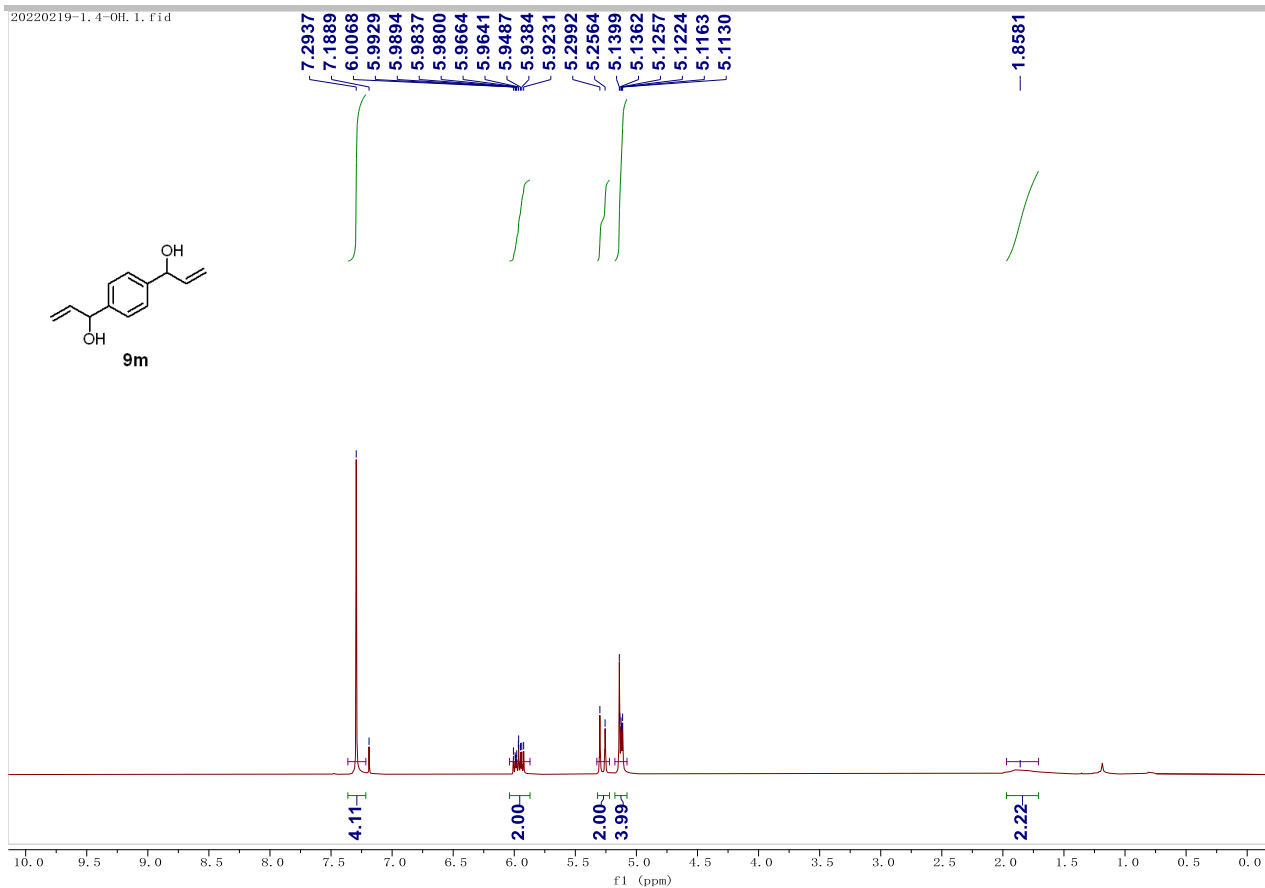


¹H NMR (400 MHz, CDCl₃) spectrum of **9I**

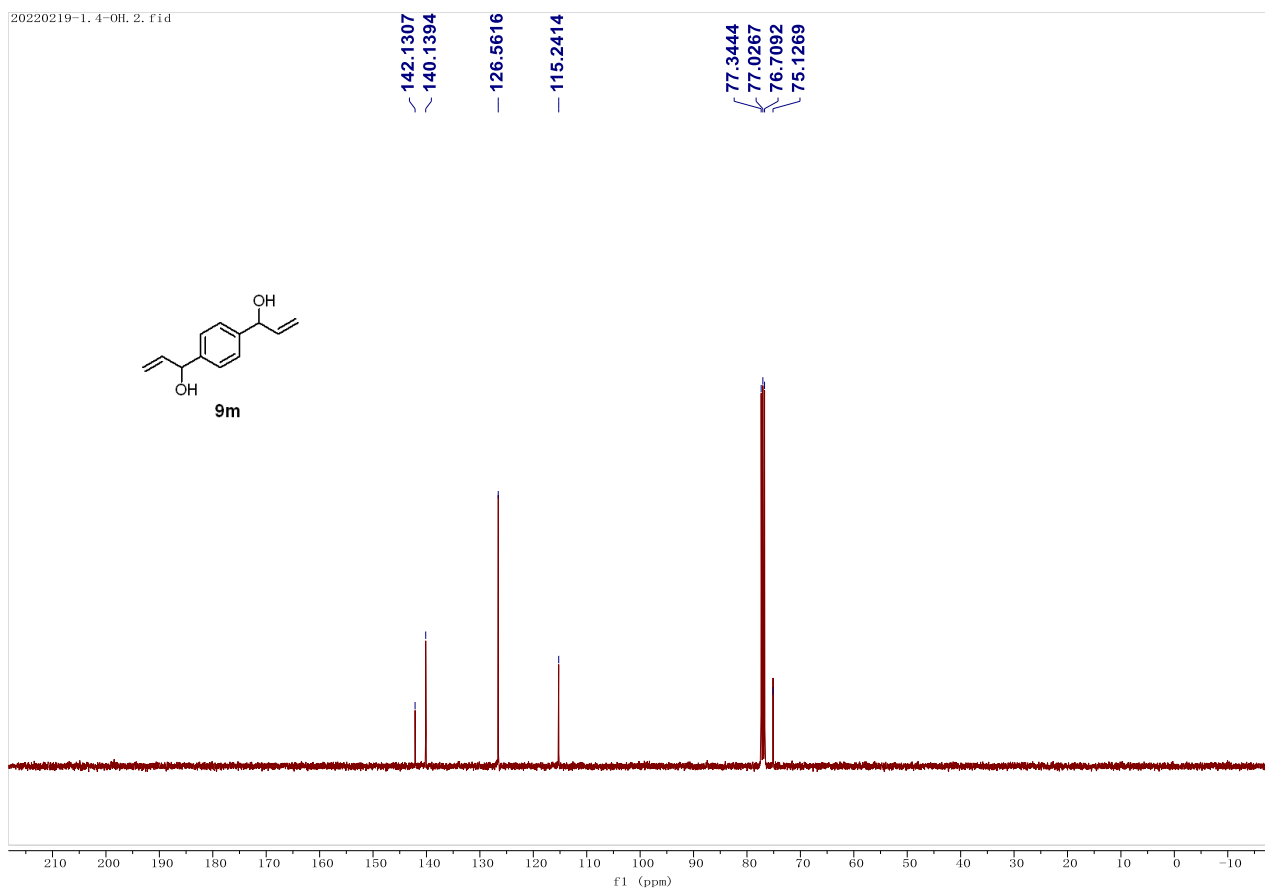


¹³C NMR (100 MHz, CDCl₃) spectrum of **9I**

SUPPORTING INFORMATION

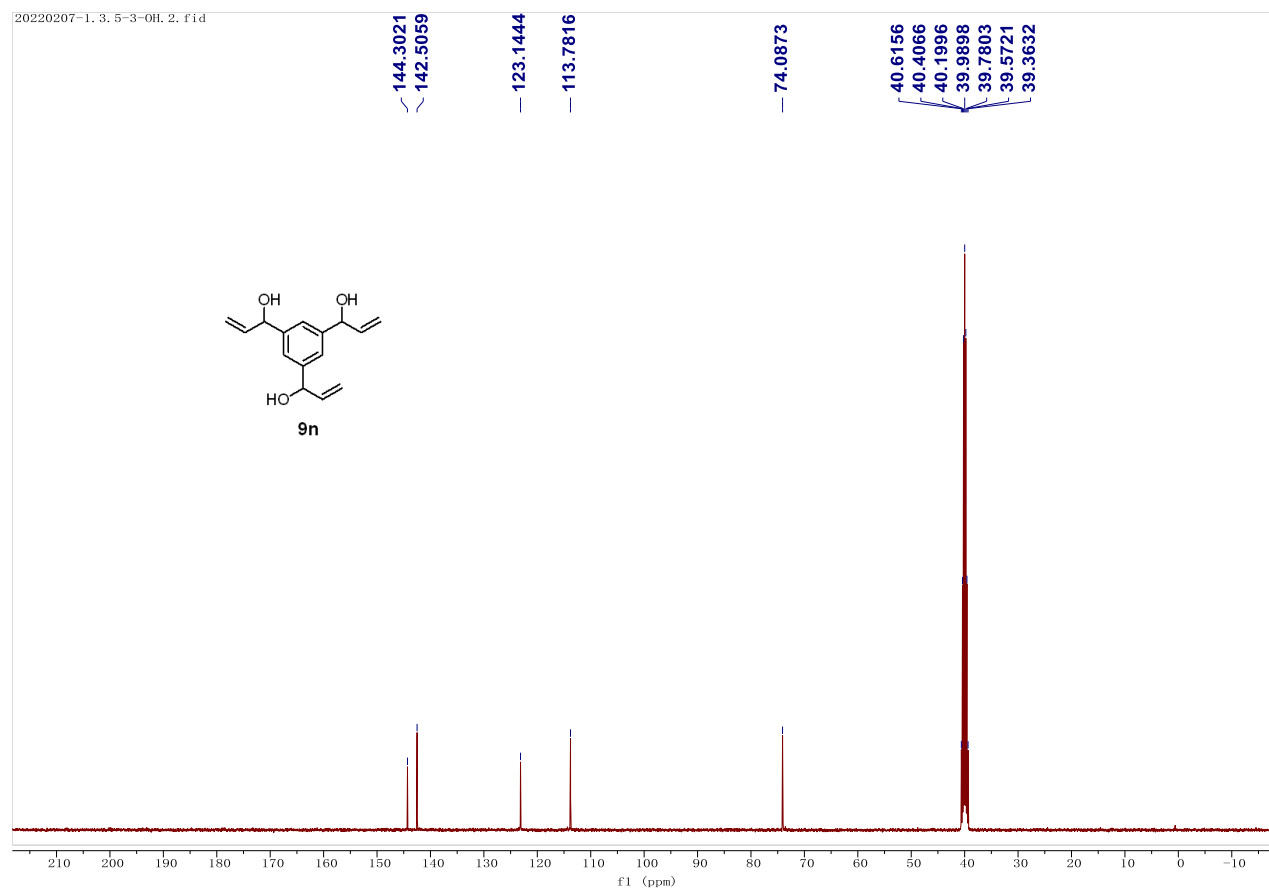
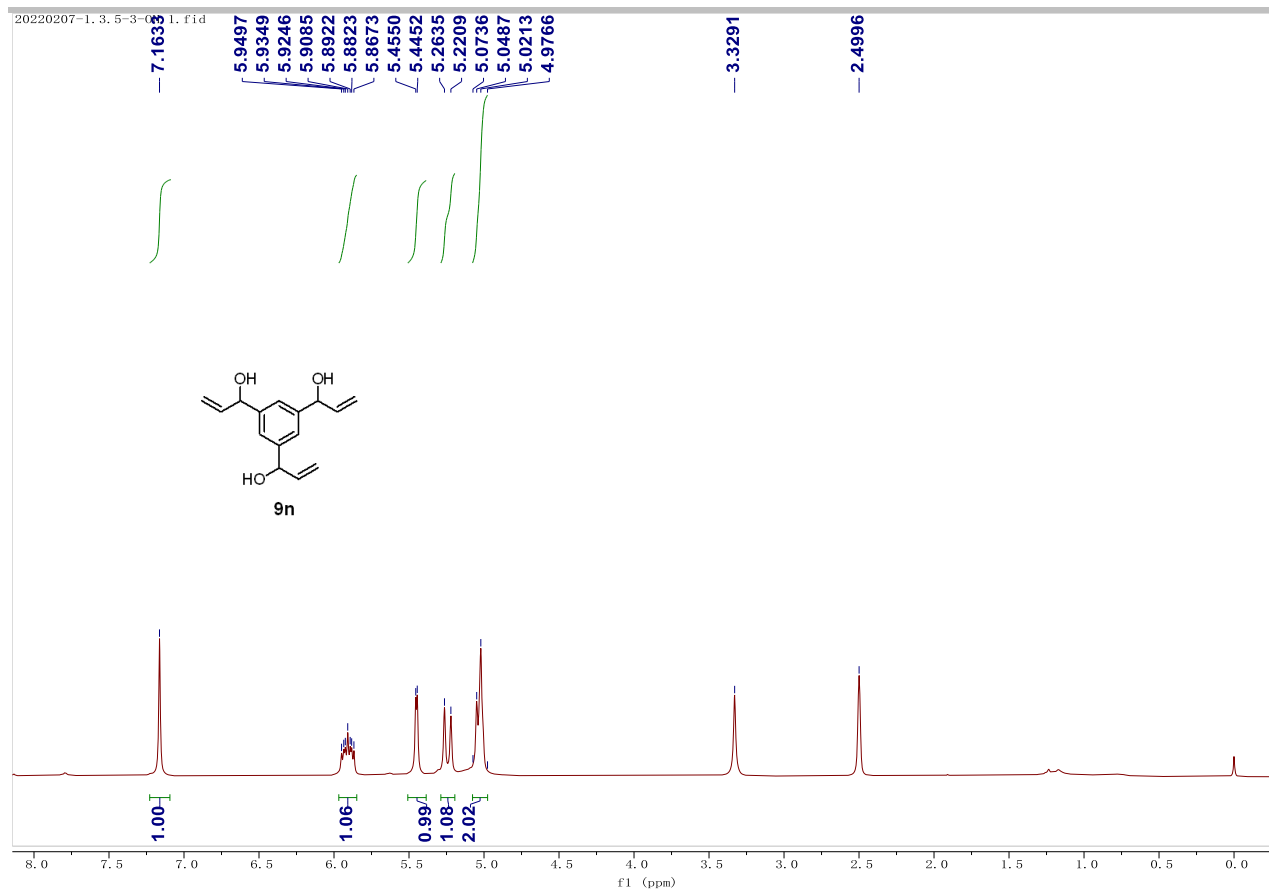


^1H NMR (400 MHz, CDCl_3) spectrum of **9m**



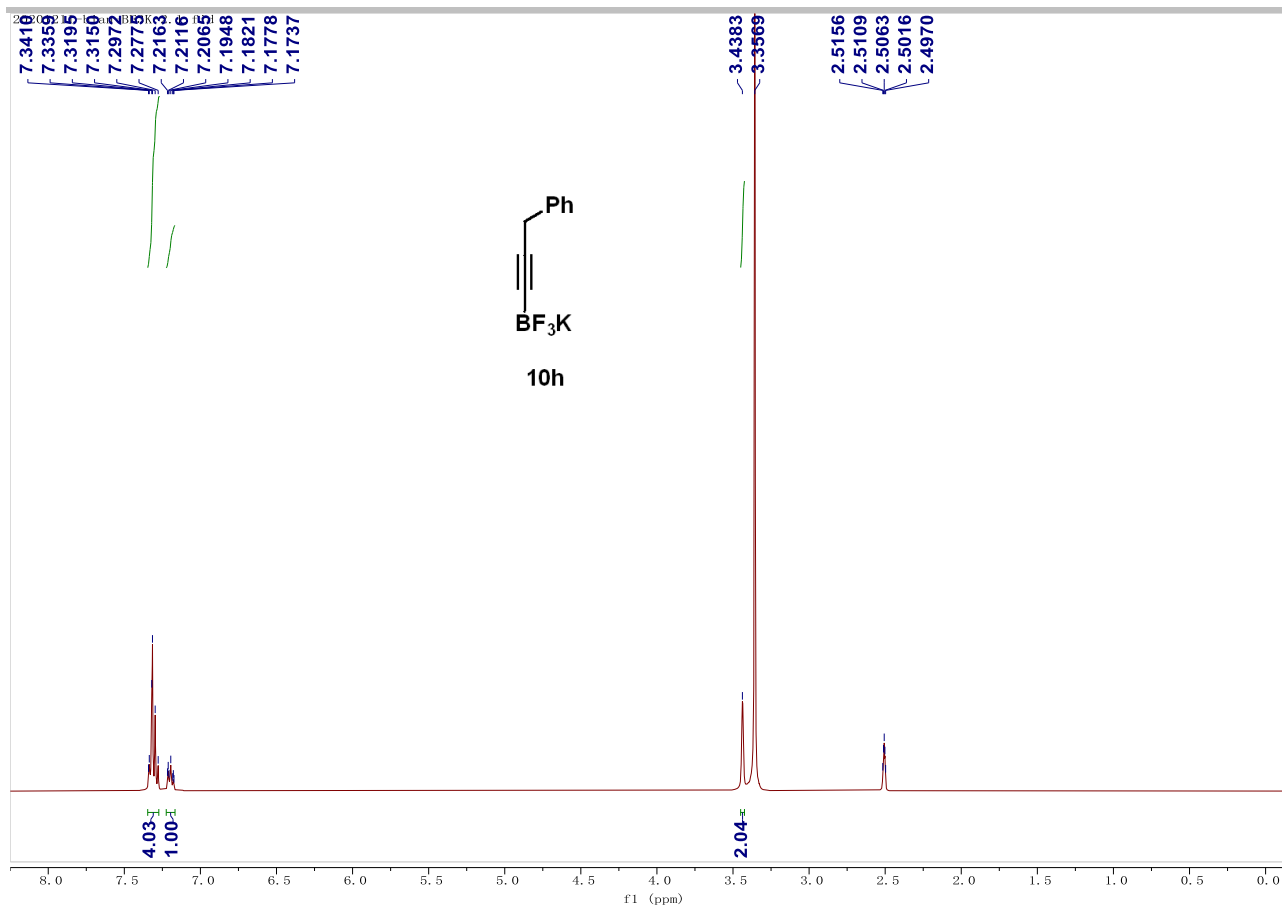
^{13}C NMR (100 MHz, CDCl_3) spectrum of **9m**

SUPPORTING INFORMATION

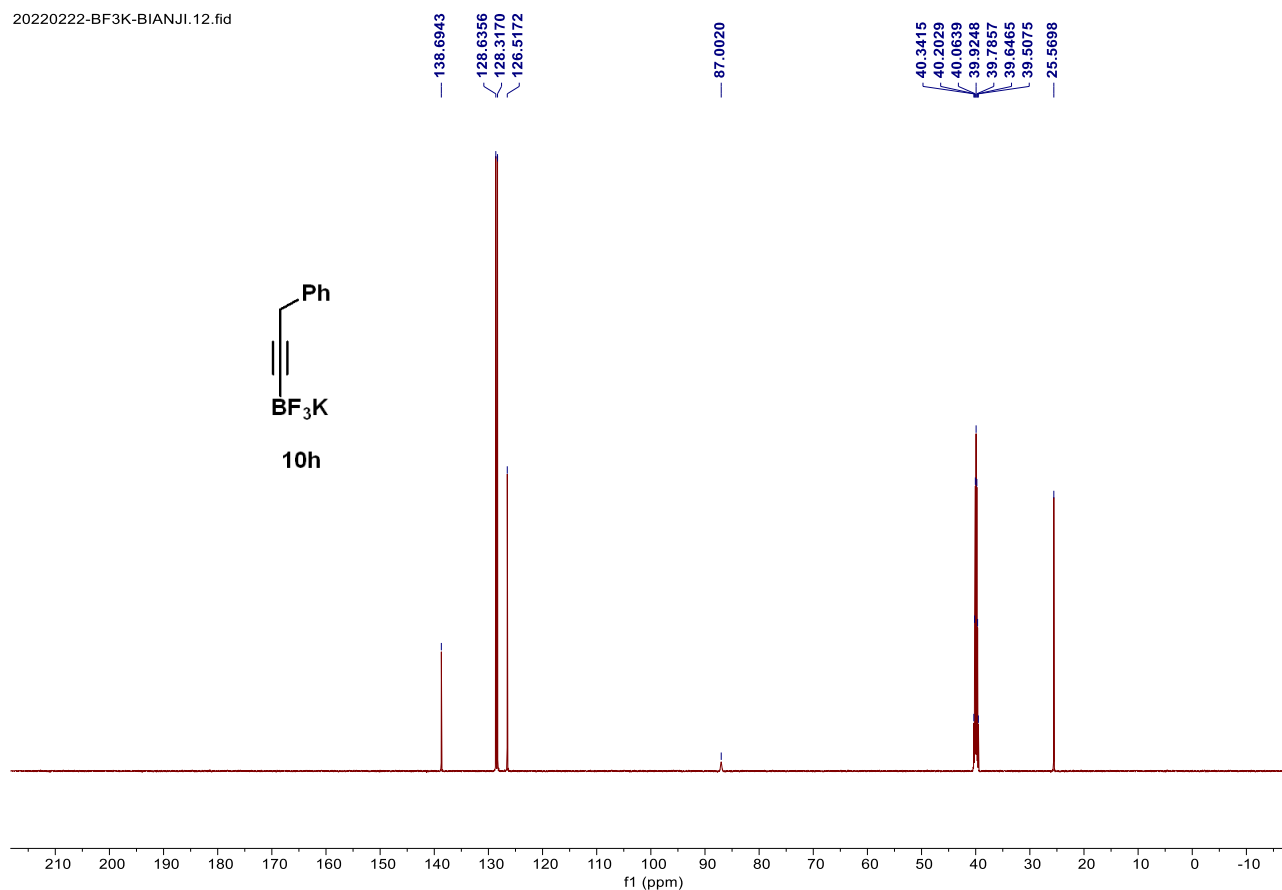


¹³C NMR (100 MHz, DMSO-*d*₆) spectrum of **9n**

SUPPORTING INFORMATION



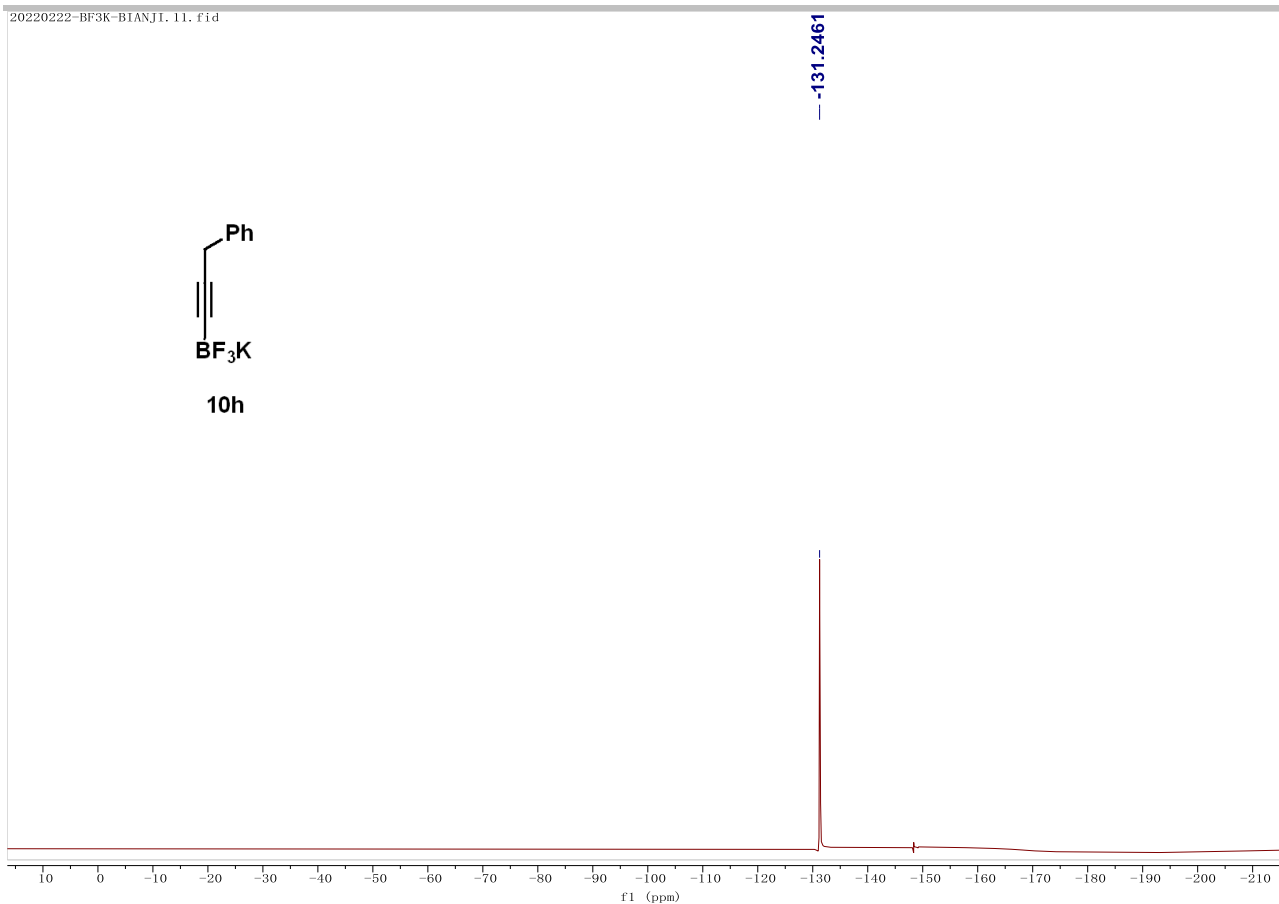
¹H NMR (400 MHz, DMSO-*d*₆) spectrum of **10h**



¹³C NMR (150 MHz, DMSO-*d*₆) spectrum of **10h**

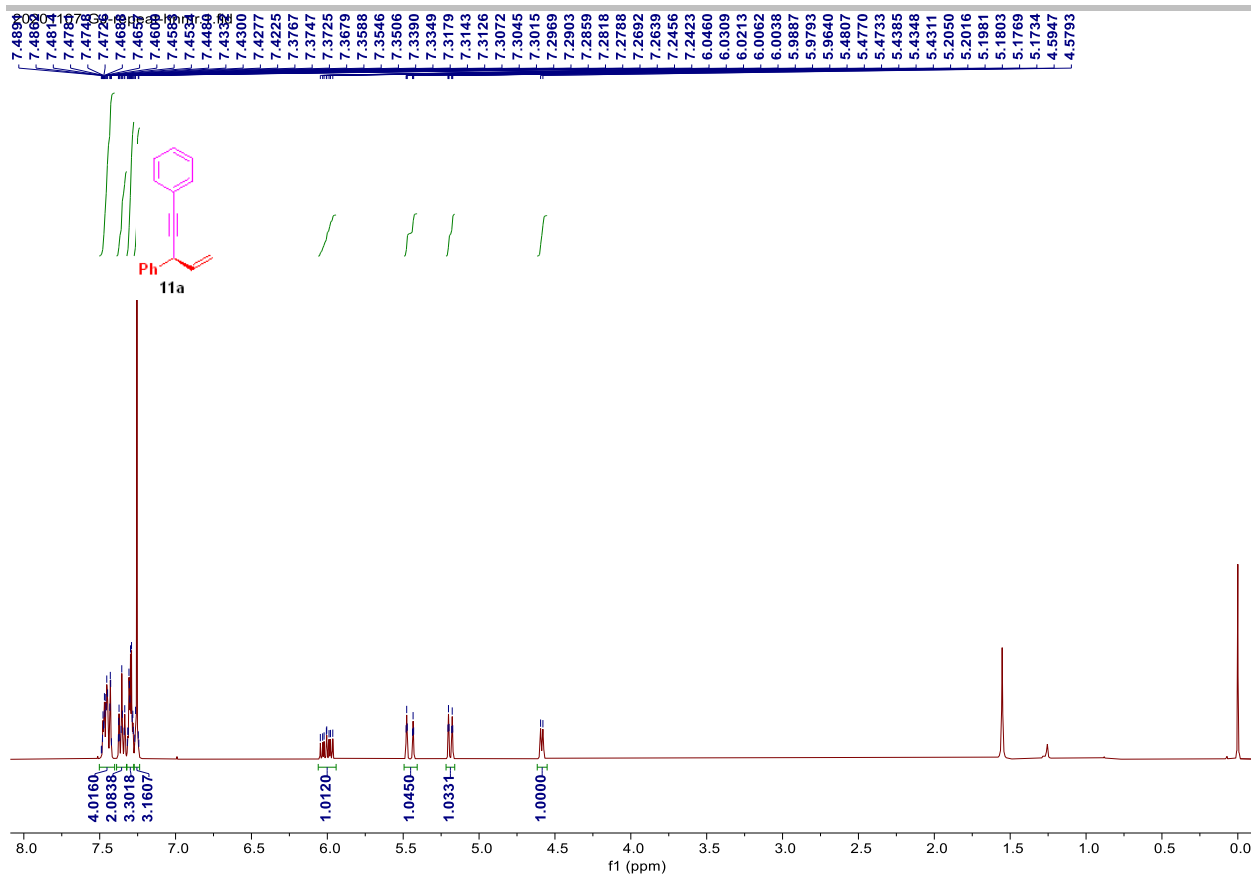
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20220222-BF3K-BIANJI.11.fid

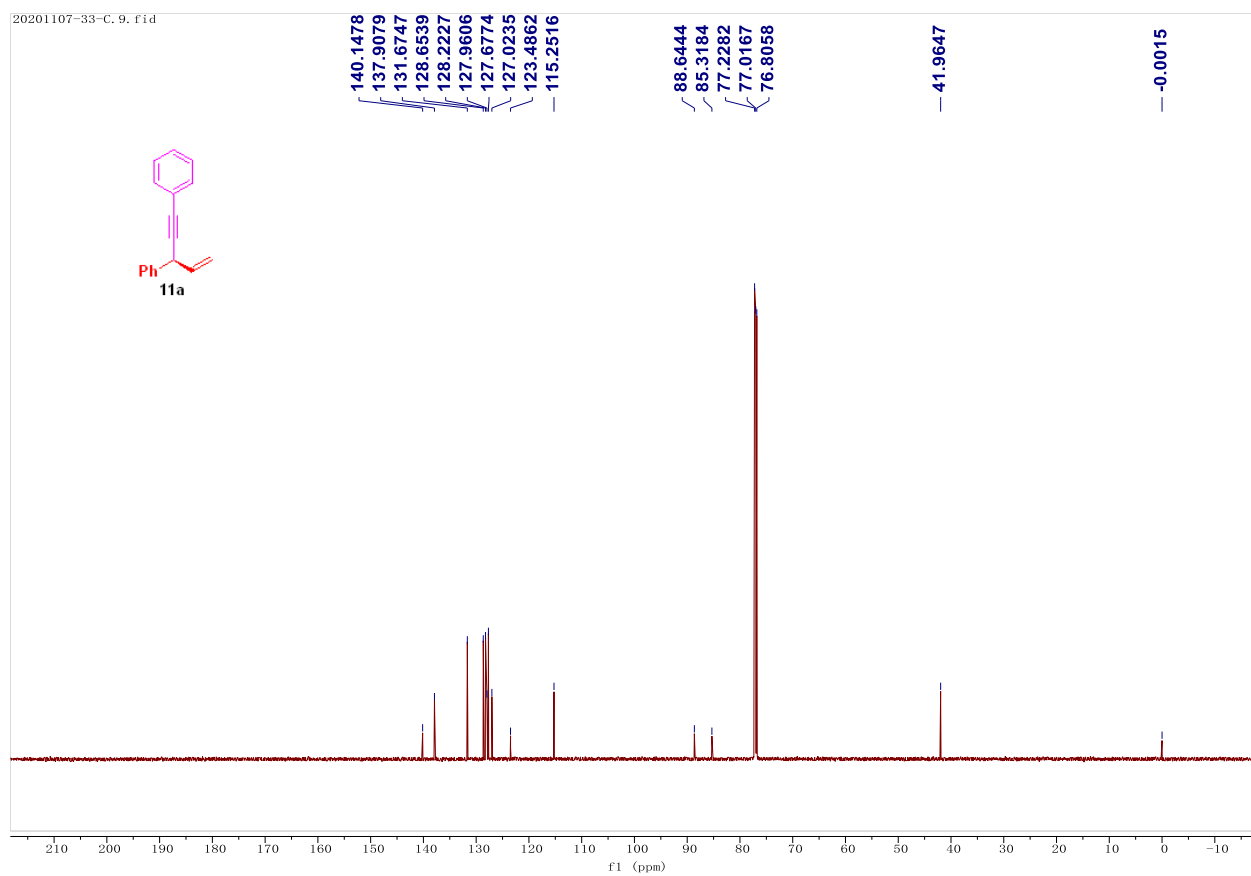


¹⁹F NMR (565 MHz, DMSO-*d*₆) spectrum of 10h

SUPPORTING INFORMATION

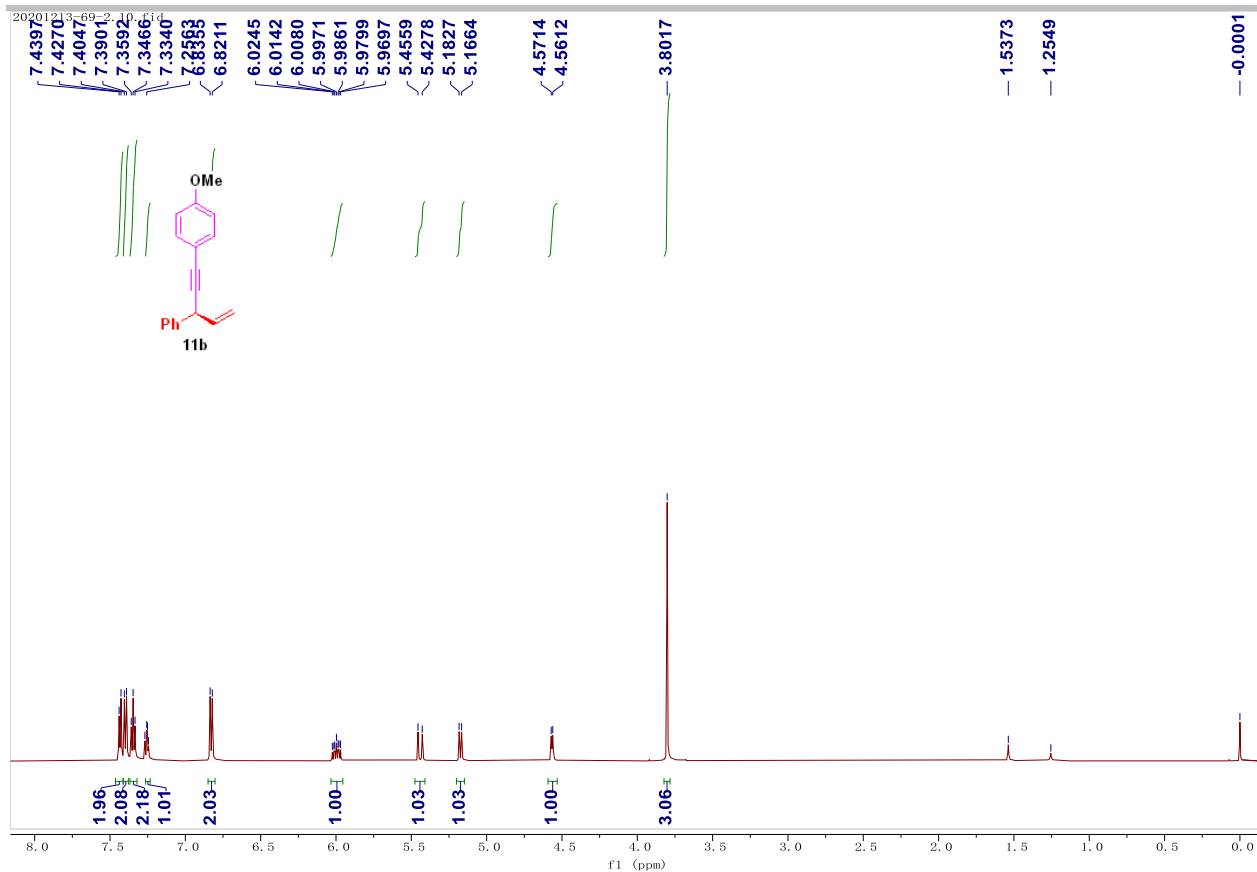


¹H NMR (400 MHz, CDCl₃) spectrum of **11a**

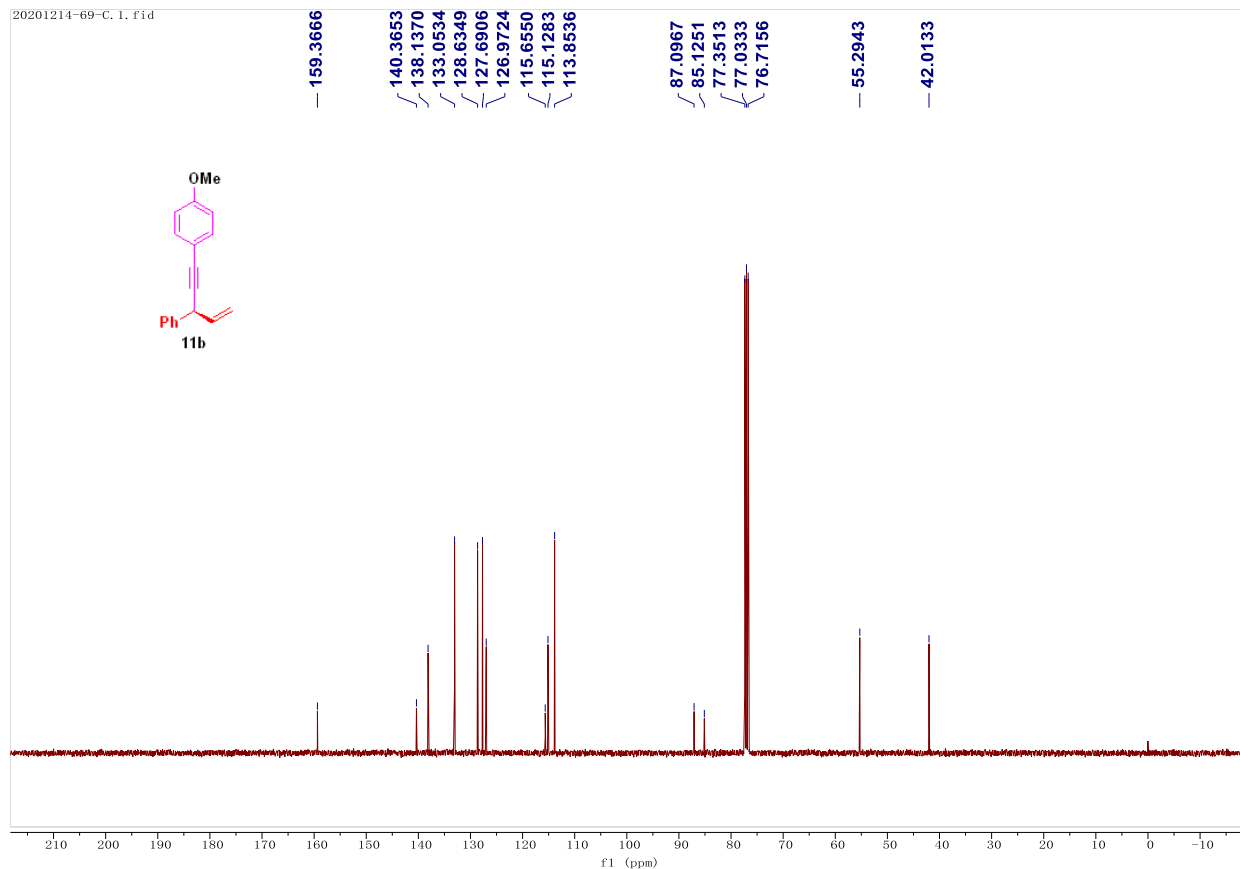


¹³C NMR (150 MHz, CDCl₃) spectrum of **11a**

SUPPORTING INFORMATION

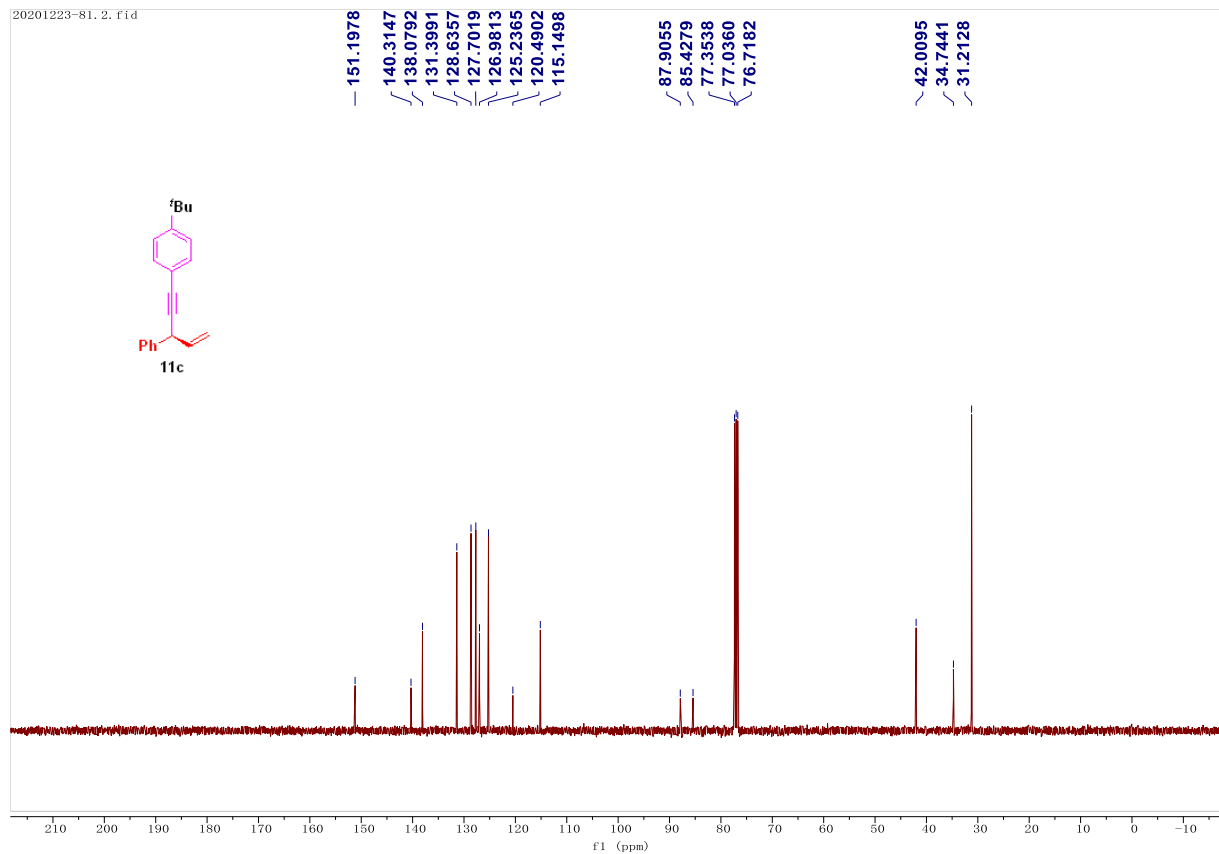
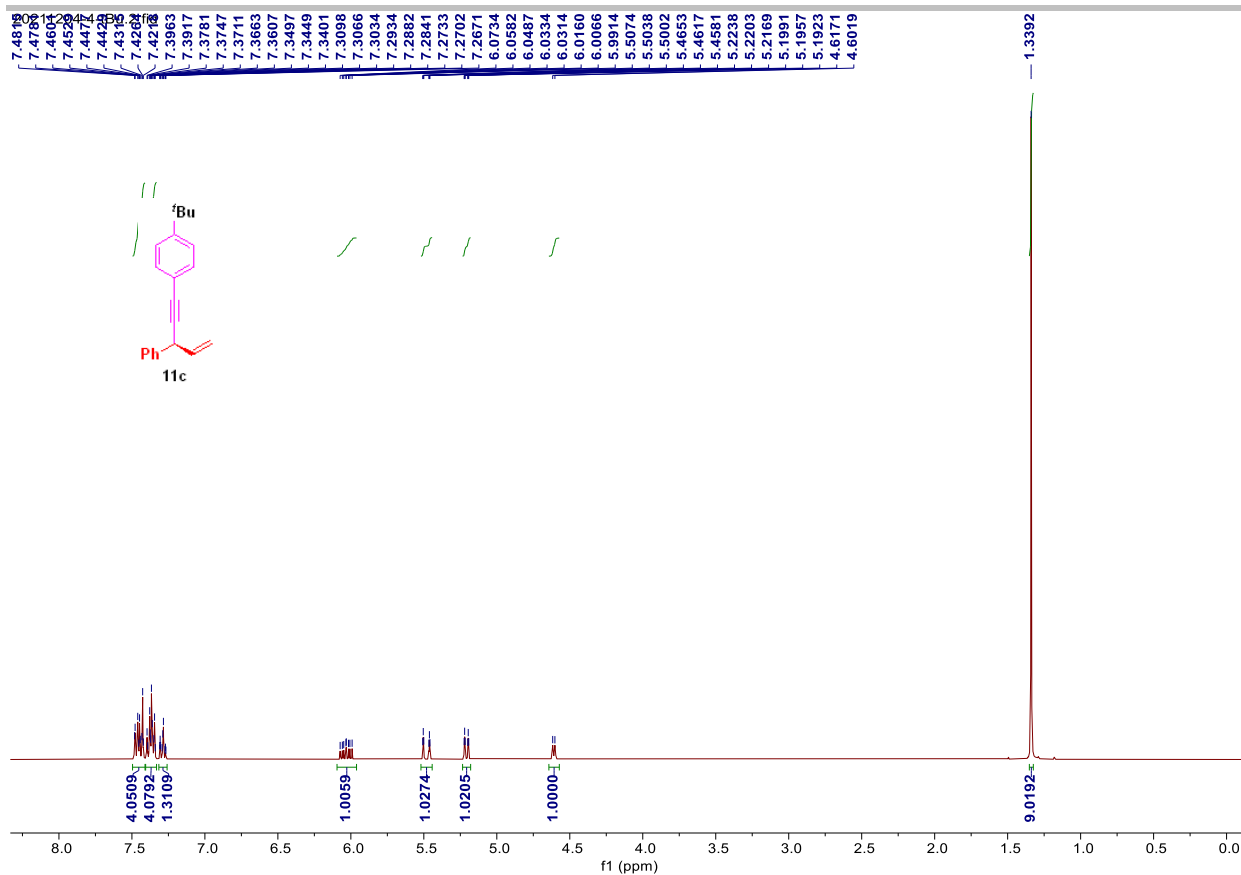


¹H NMR (600 MHz, CDCl₃) spectrum of **11b**

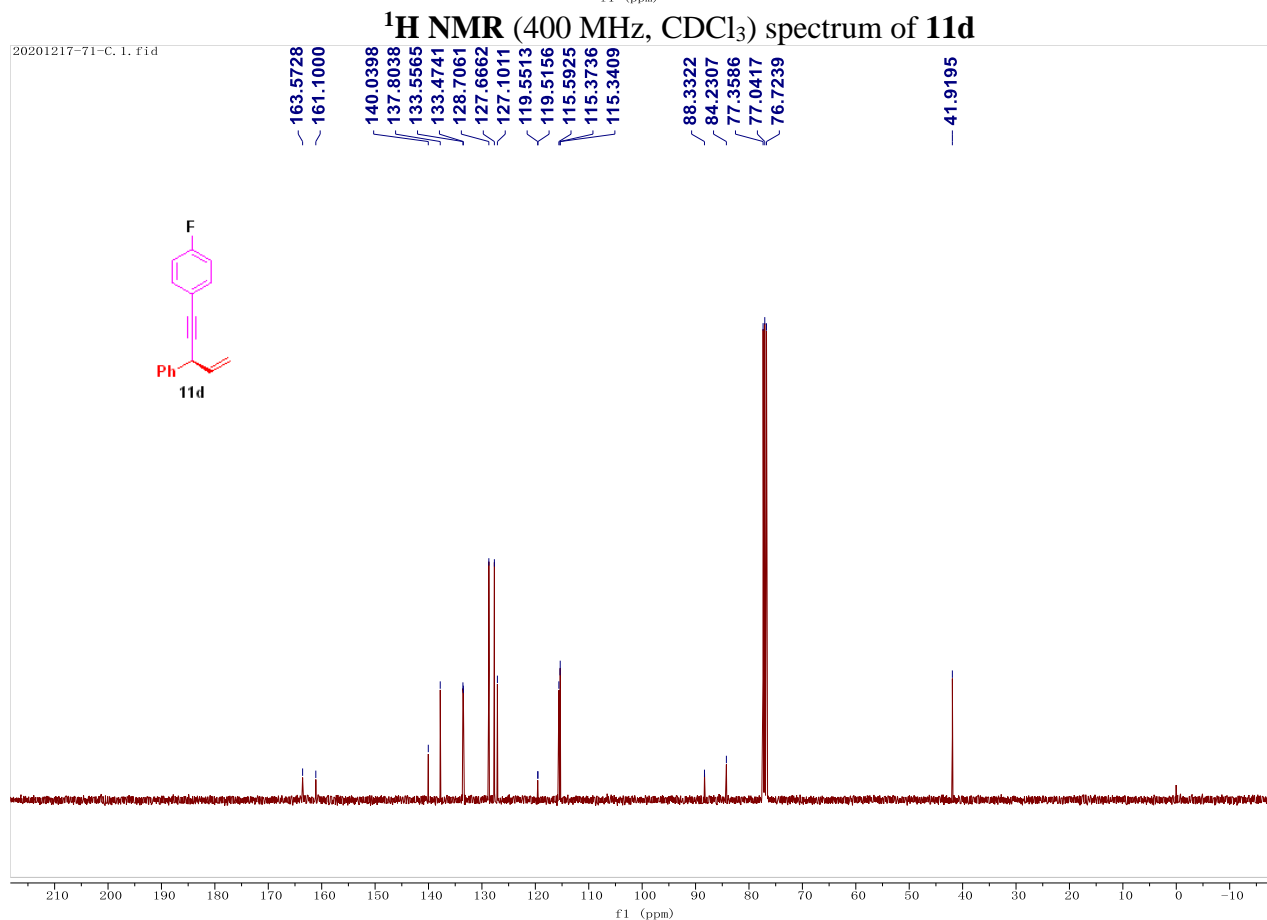
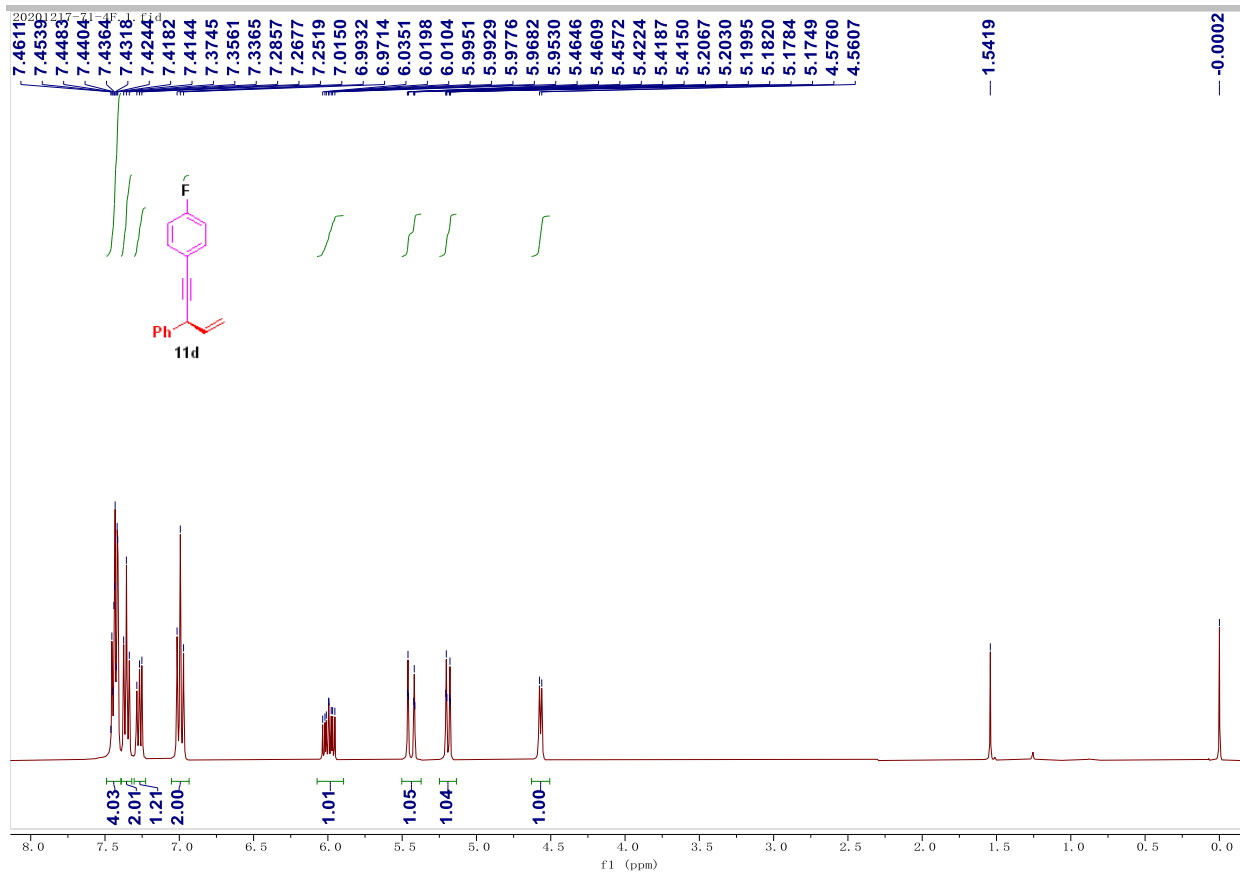


¹³C NMR (100 MHz, CDCl₃) spectrum of **11b**

SUPPORTING INFORMATION

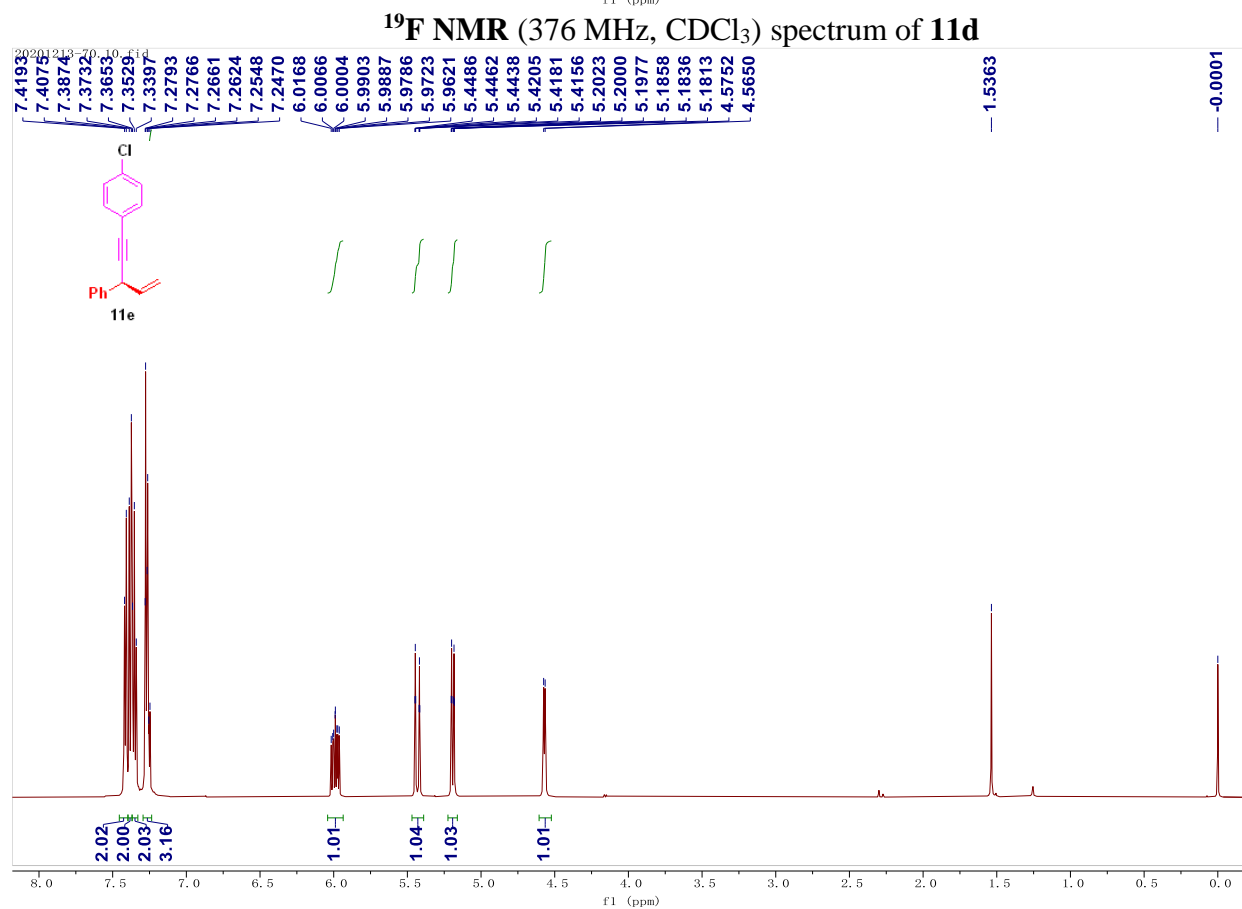
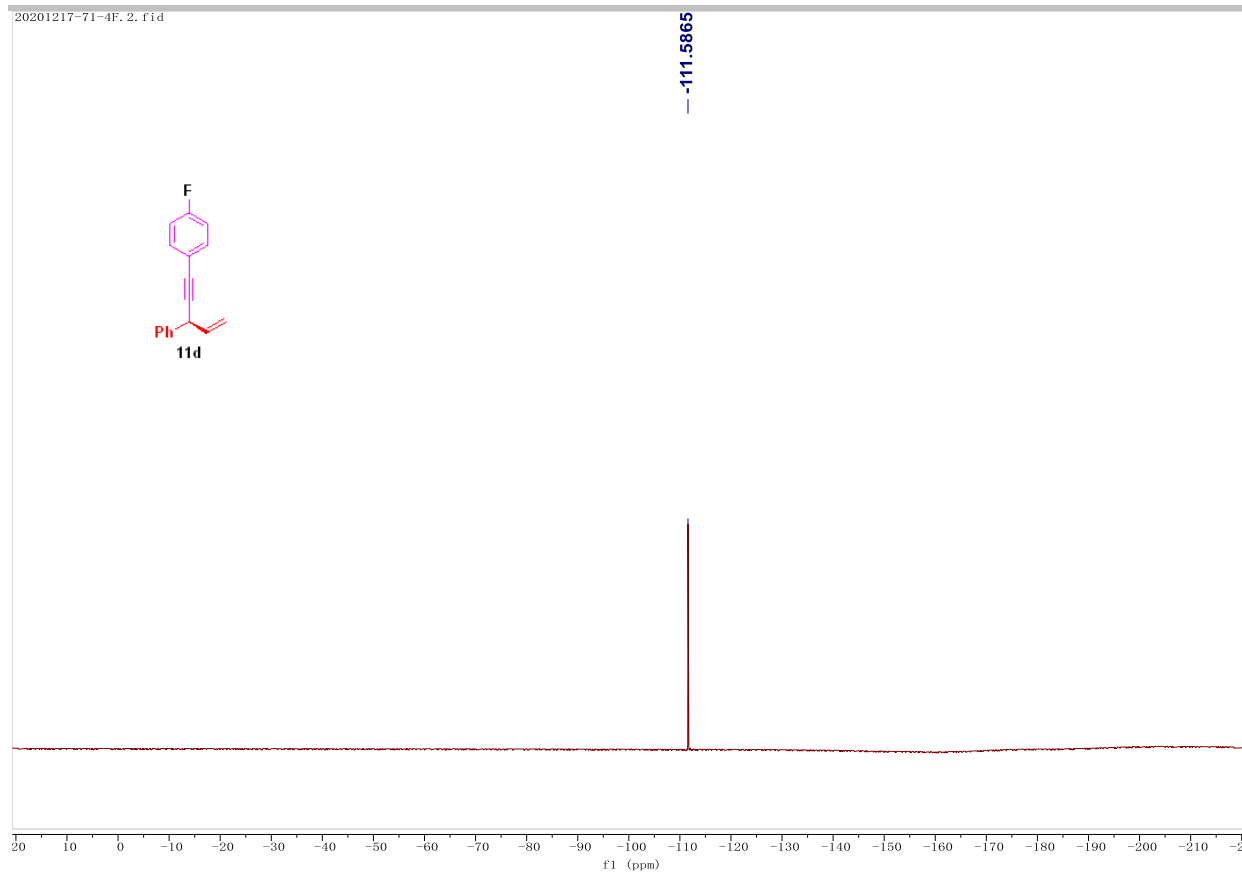


SUPPORTING INFORMATION

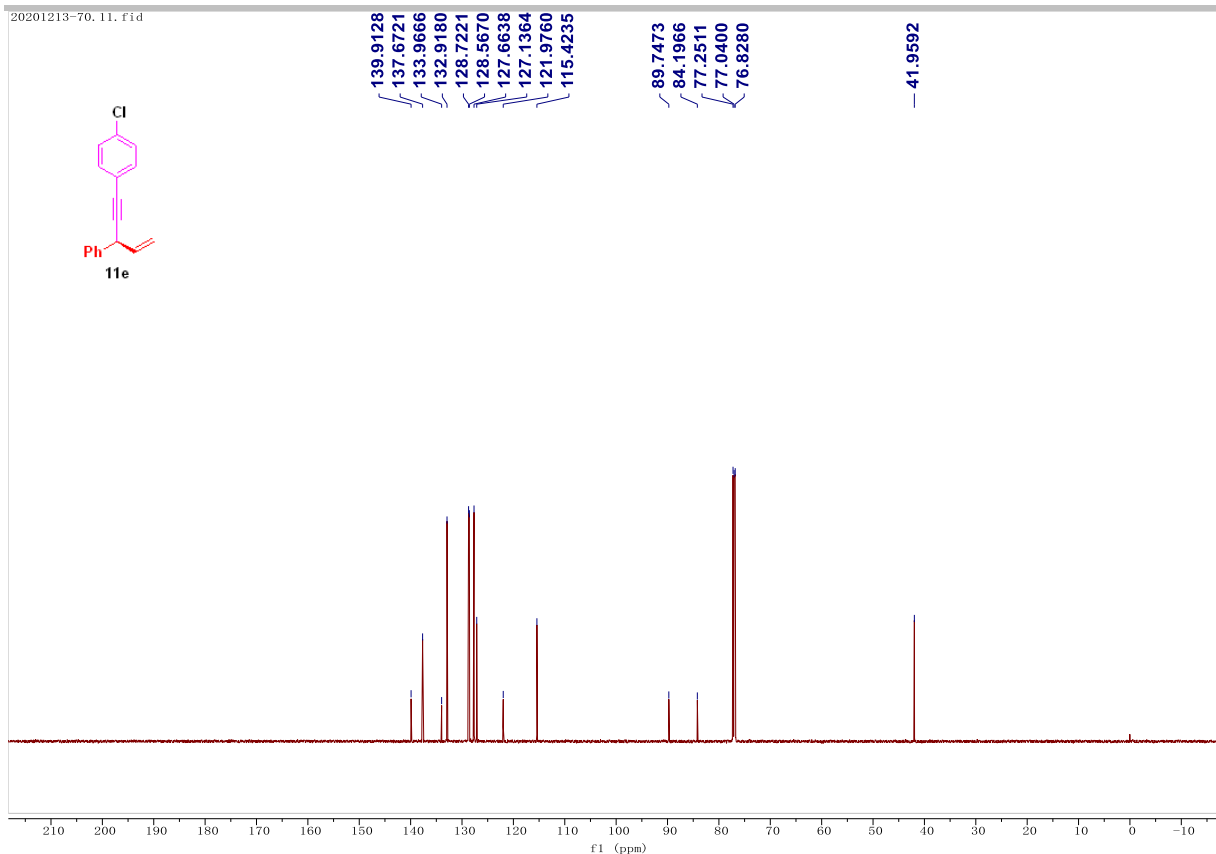


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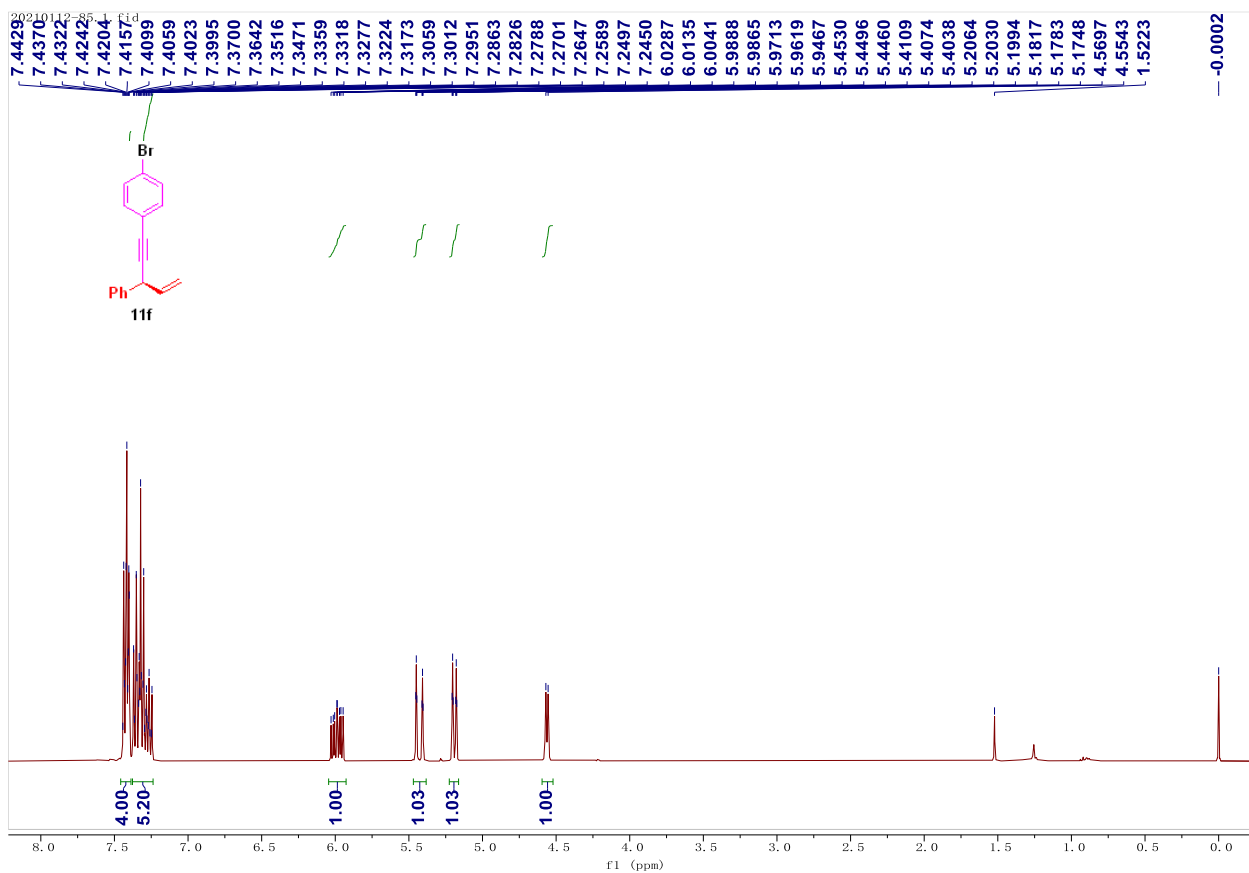
20201217-71-4F.2.fid



SUPPORTING INFORMATION

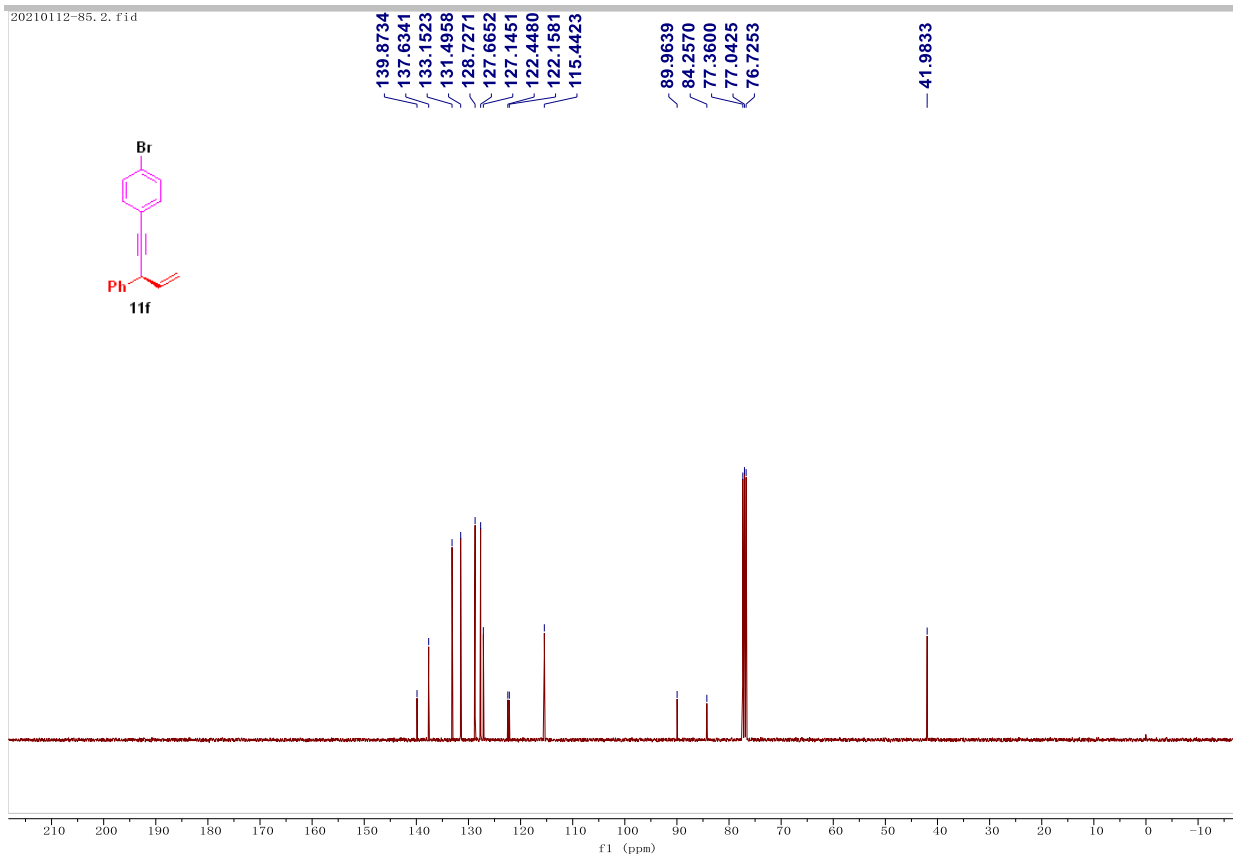


^{13}C NMR (150 MHz, CDCl_3) spectrum of **11e**

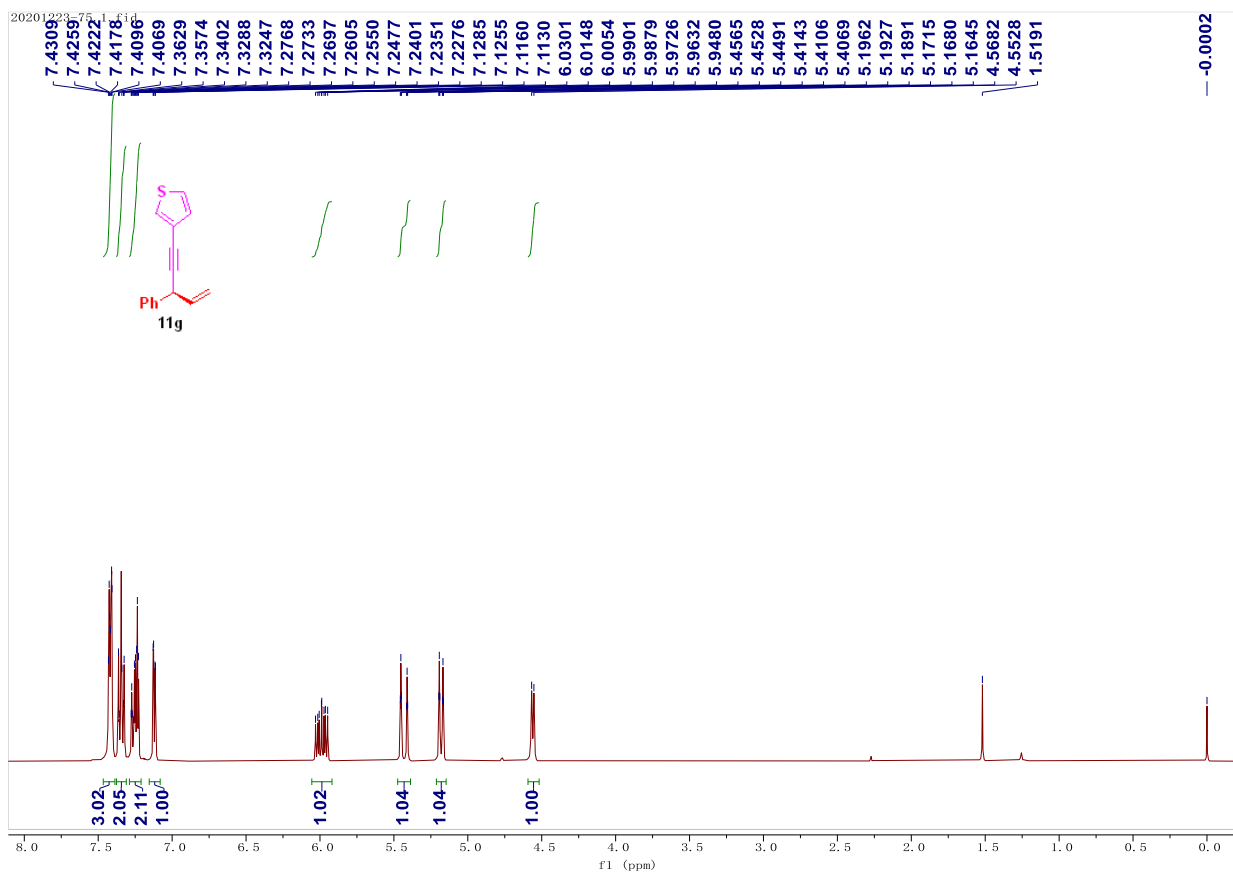


^1H NMR (400 MHz, CDCl_3) spectrum of **11f**

SUPPORTING INFORMATION



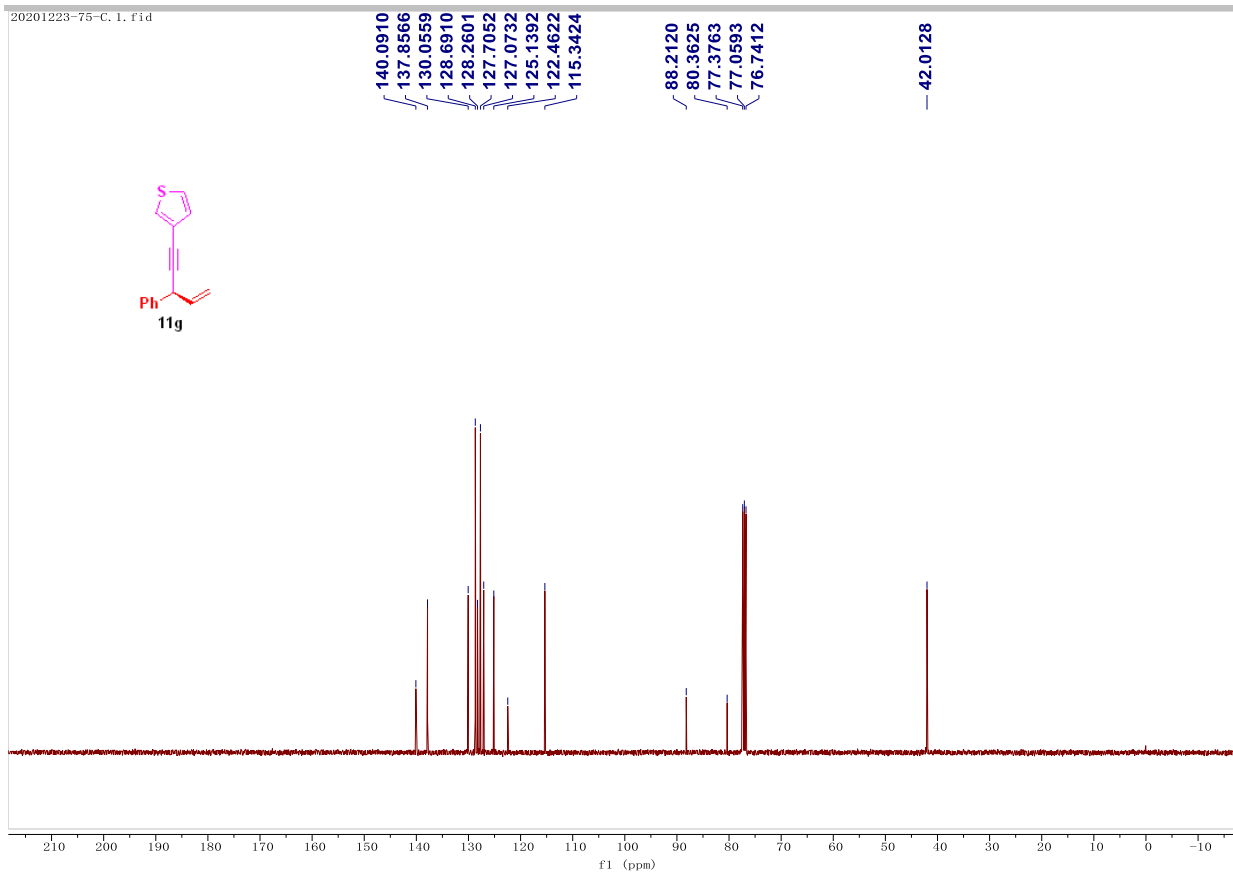
¹³C NMR (100 MHz, CDCl₃) spectrum of **11f**



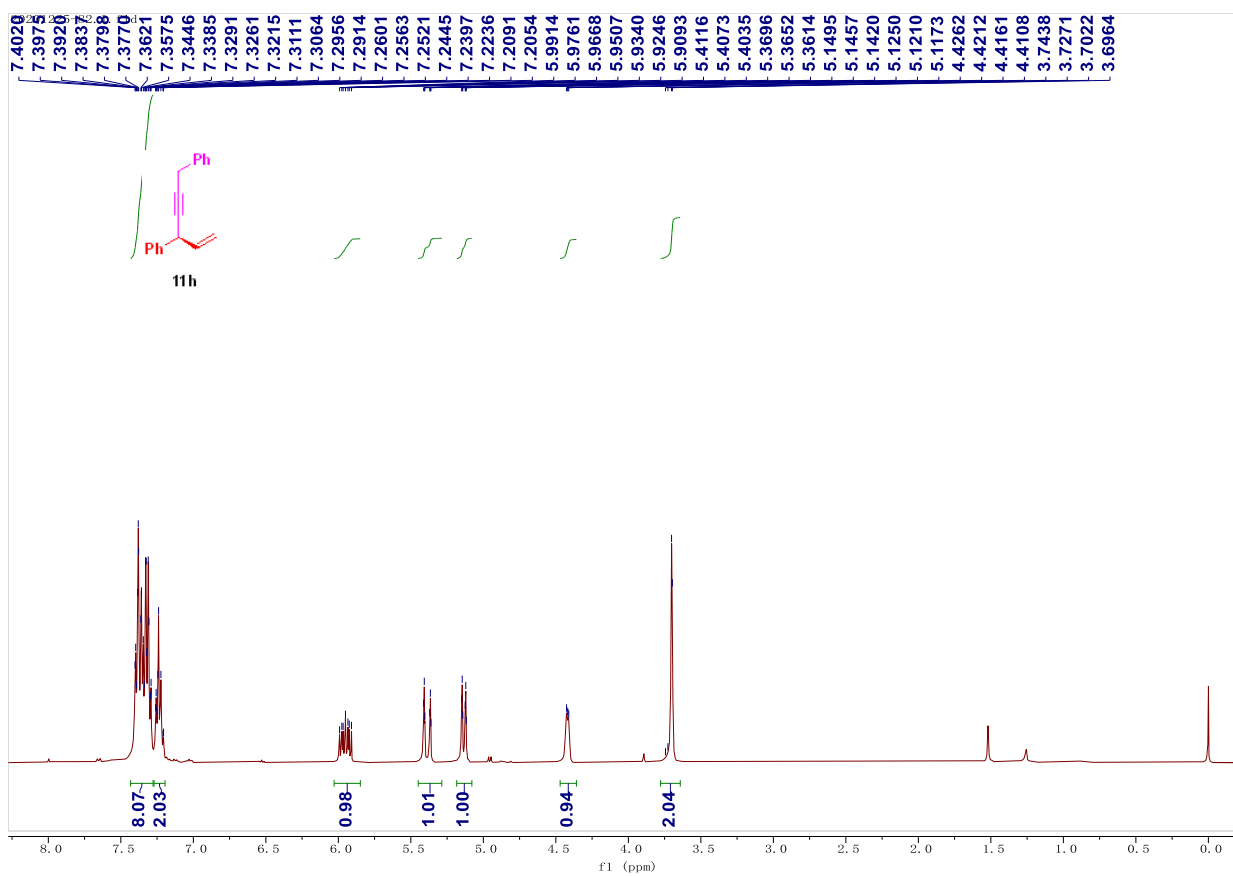
¹H NMR (400 MHz, CDCl₃) spectrum of **11g**

SUPPORTING INFORMATION

20201223-75-c. 1. fid

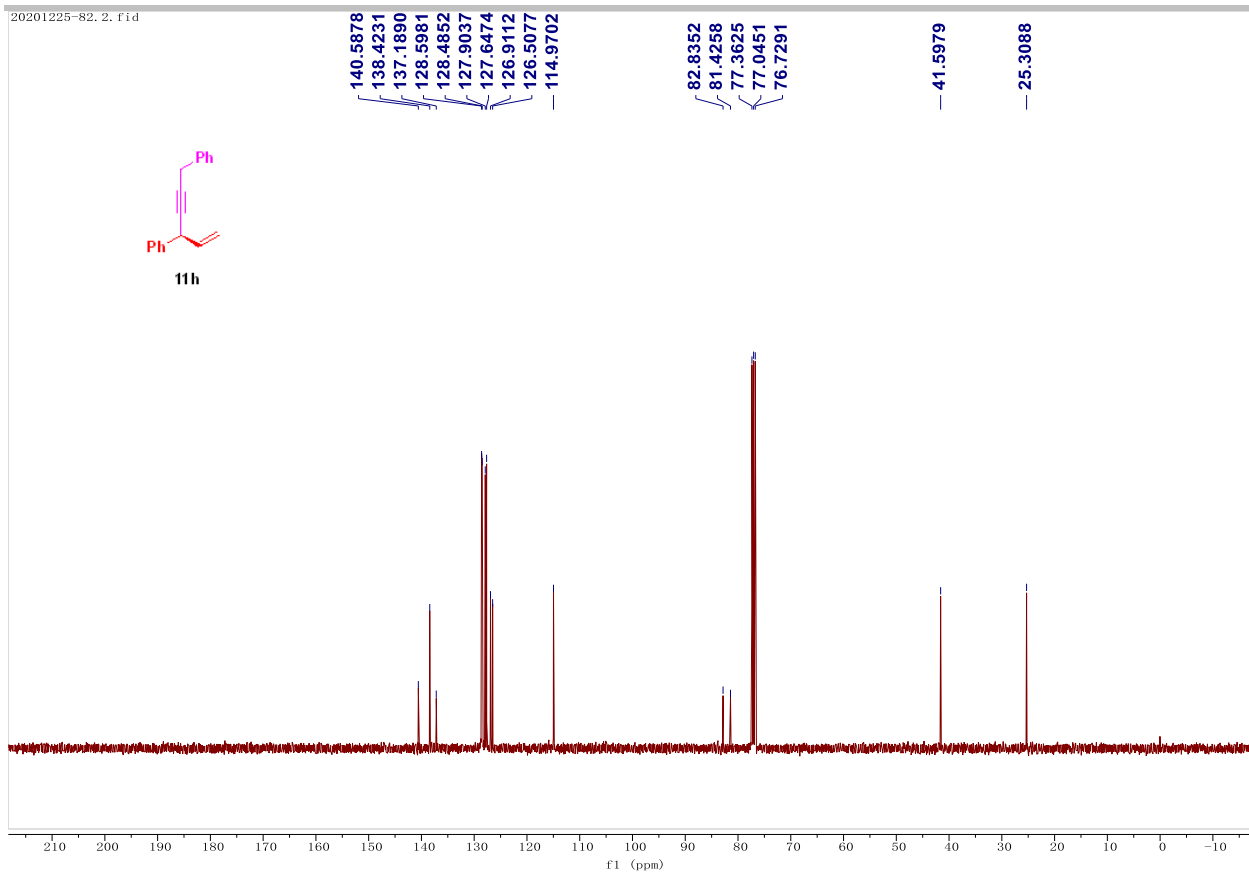


¹³C NMR (100 MHz, CDCl₃) spectrum of **11g**

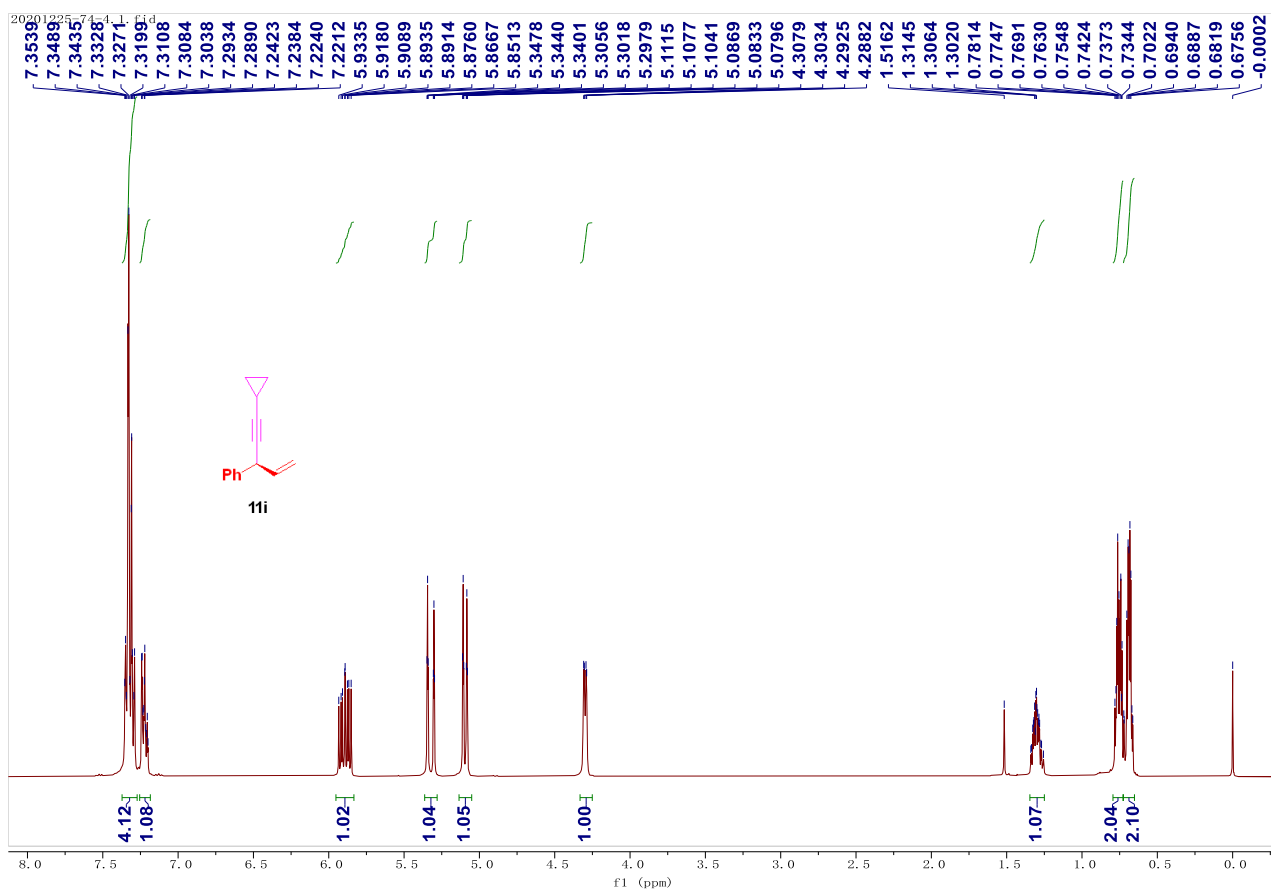


¹H NMR (400 MHz, CDCl₃) spectrum of **11h**

SUPPORTING INFORMATION



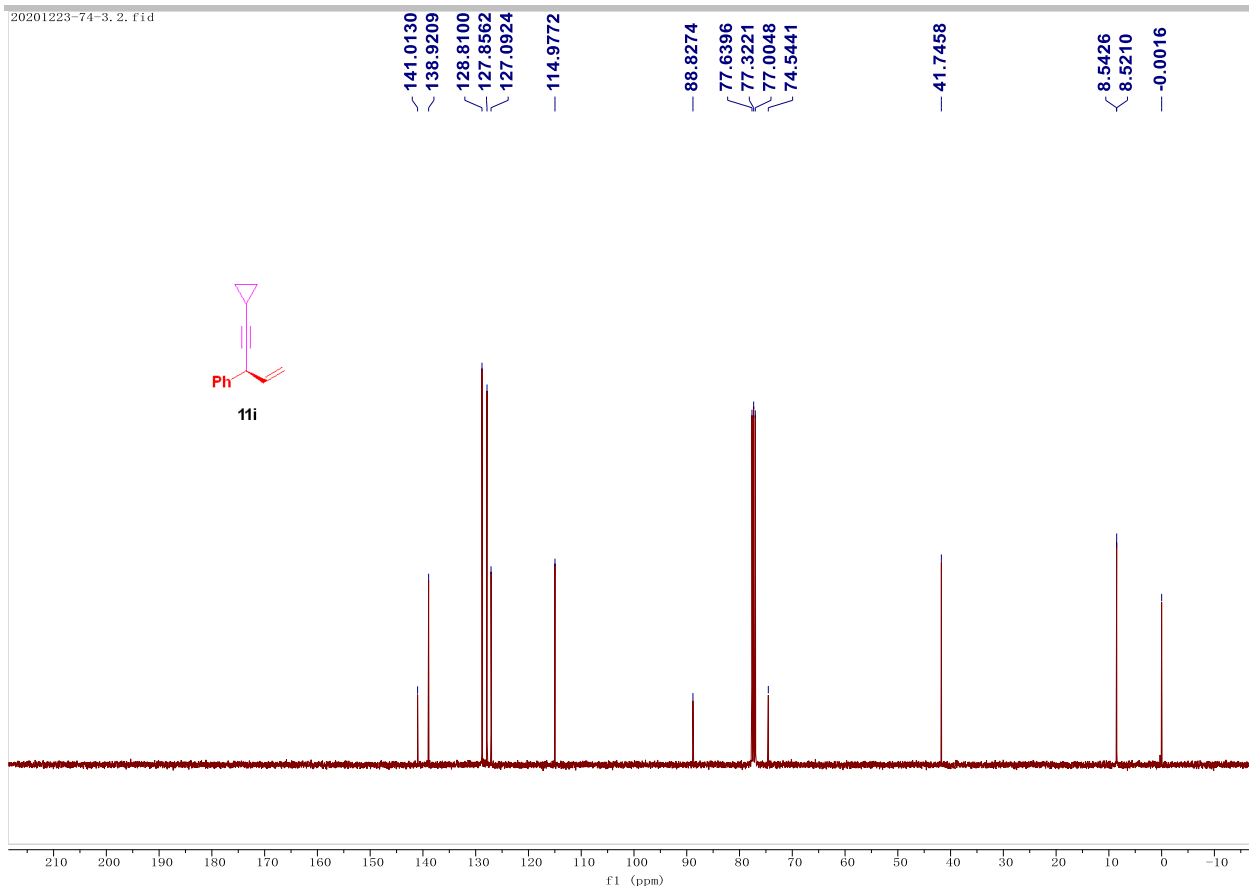
¹³C NMR (100 MHz, CDCl₃) spectrum of **11h**



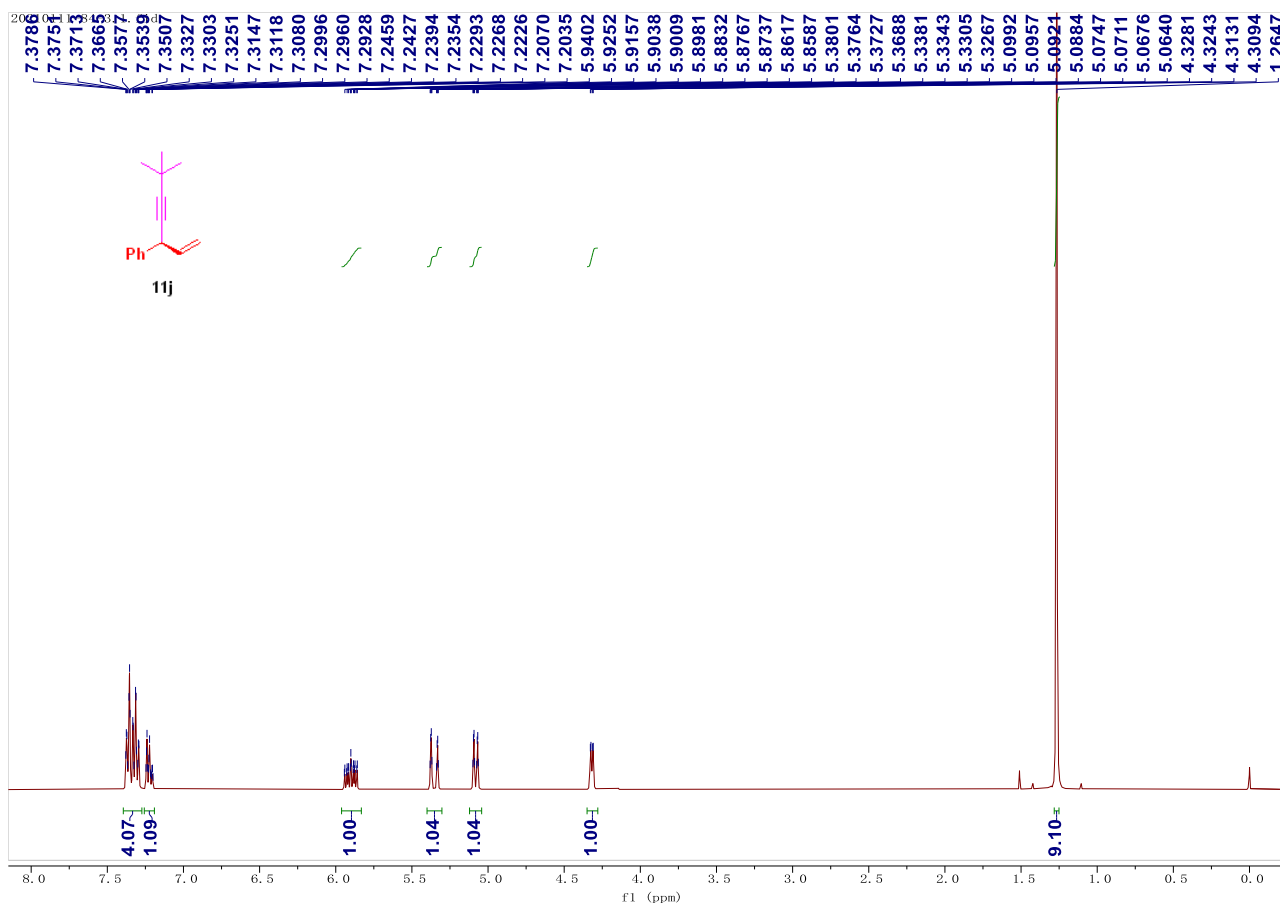
¹H NMR (400 MHz, CDCl₃) spectrum of **11i**

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20201223-74-3, 2, Fid

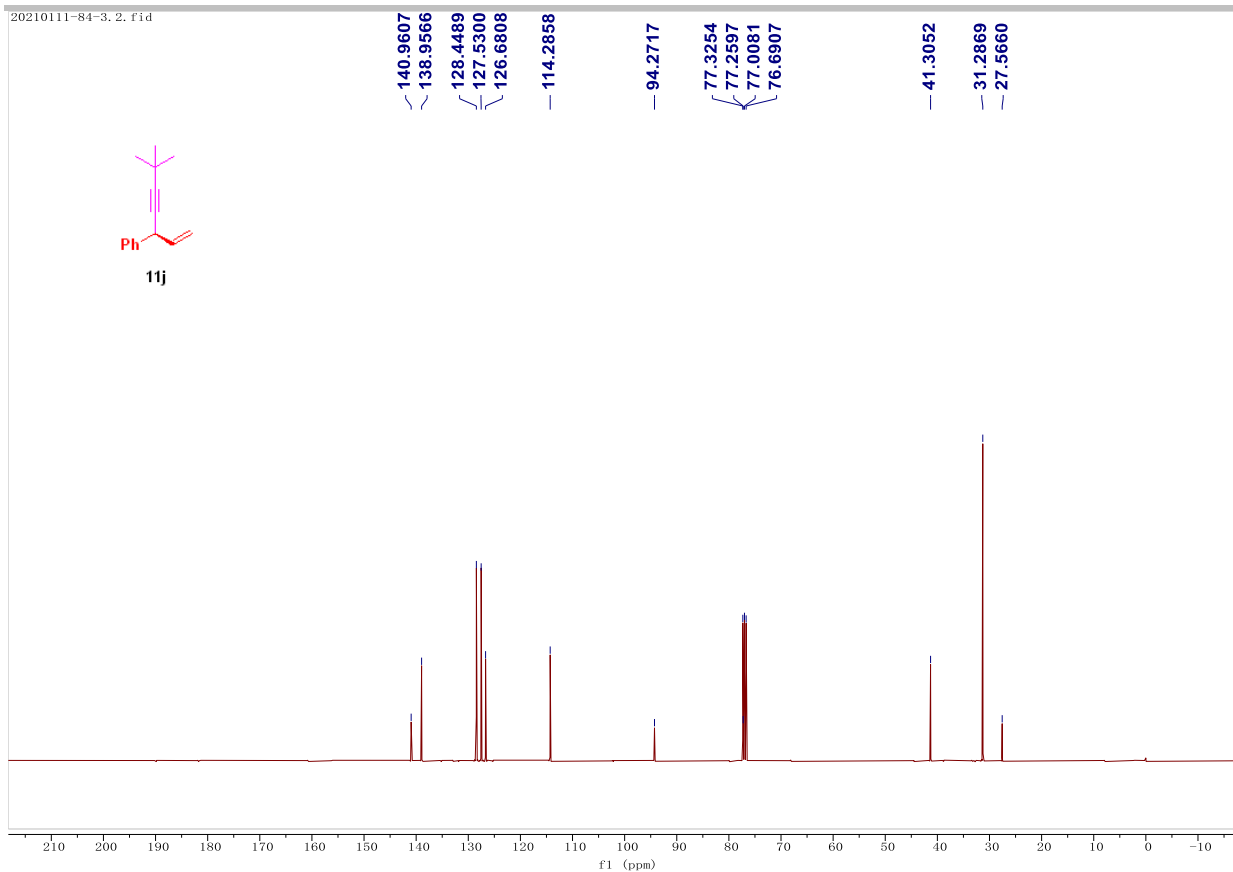


¹³C NMR (100 MHz, CDCl₃) spectrum of 11i

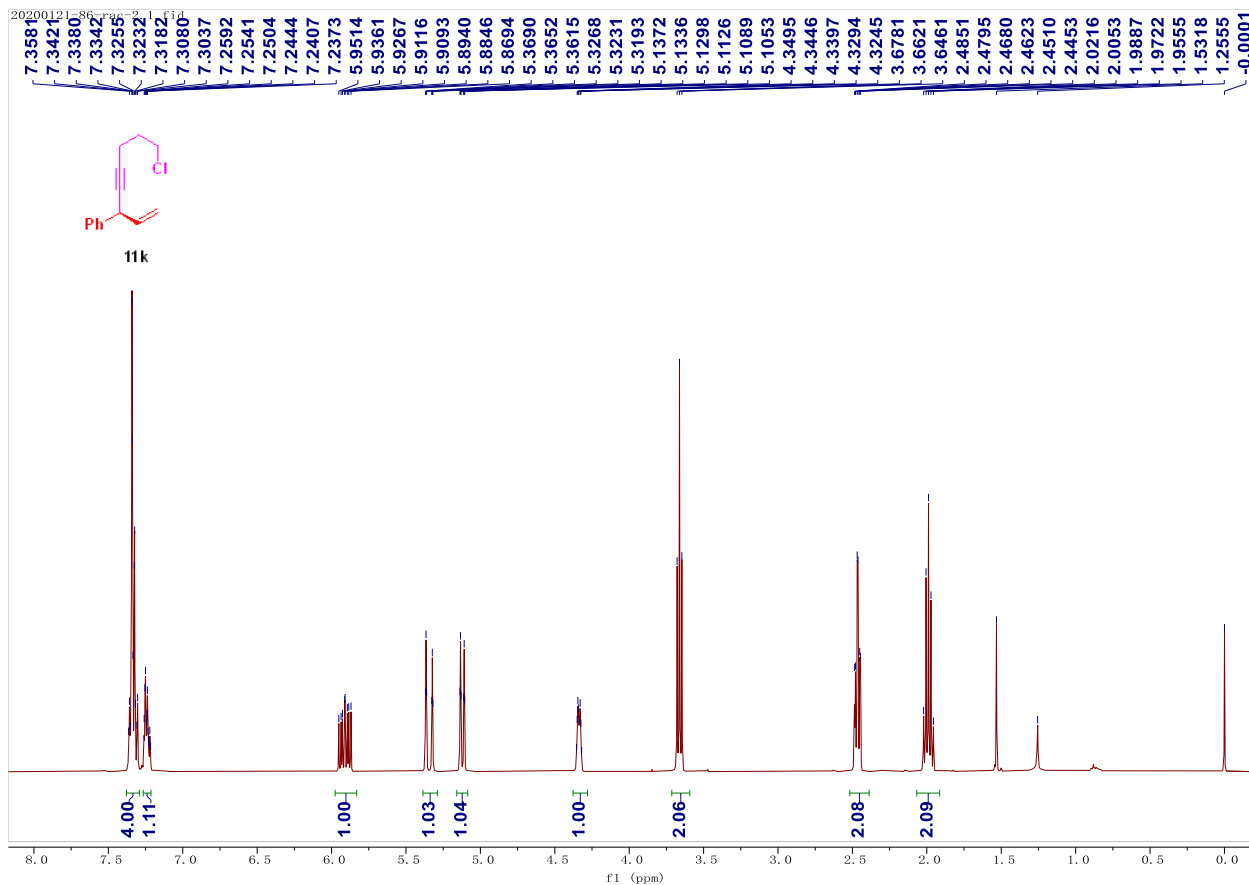


¹H NMR (400 MHz, CDCl₃) spectrum of 11j

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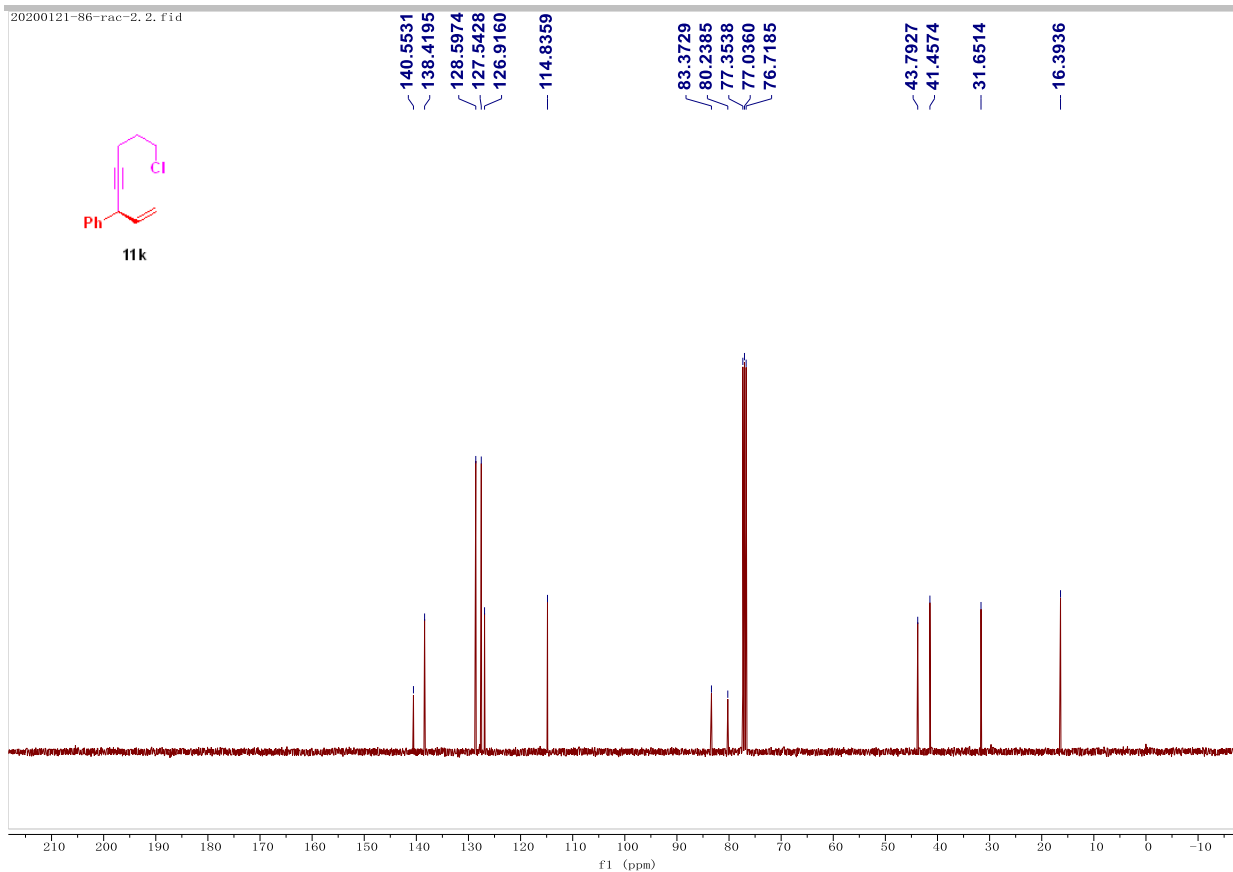
¹³C NMR (100 MHz, CDCl₃) spectrum of **11j**



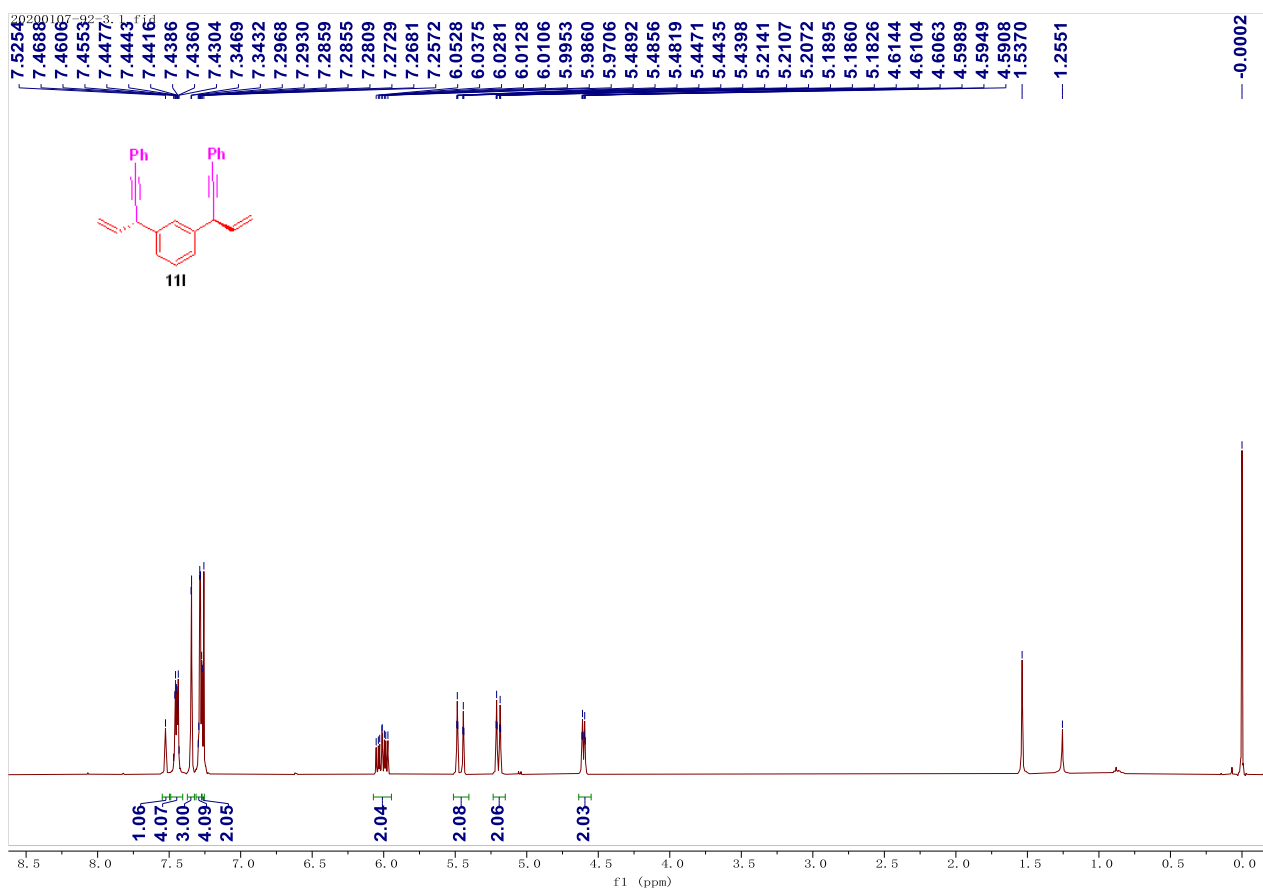
¹H NMR (400 MHz, CDCl₃) spectrum of **11k**

SUPPORTING INFORMATION

20200121-86-rac-2. 2. f1d

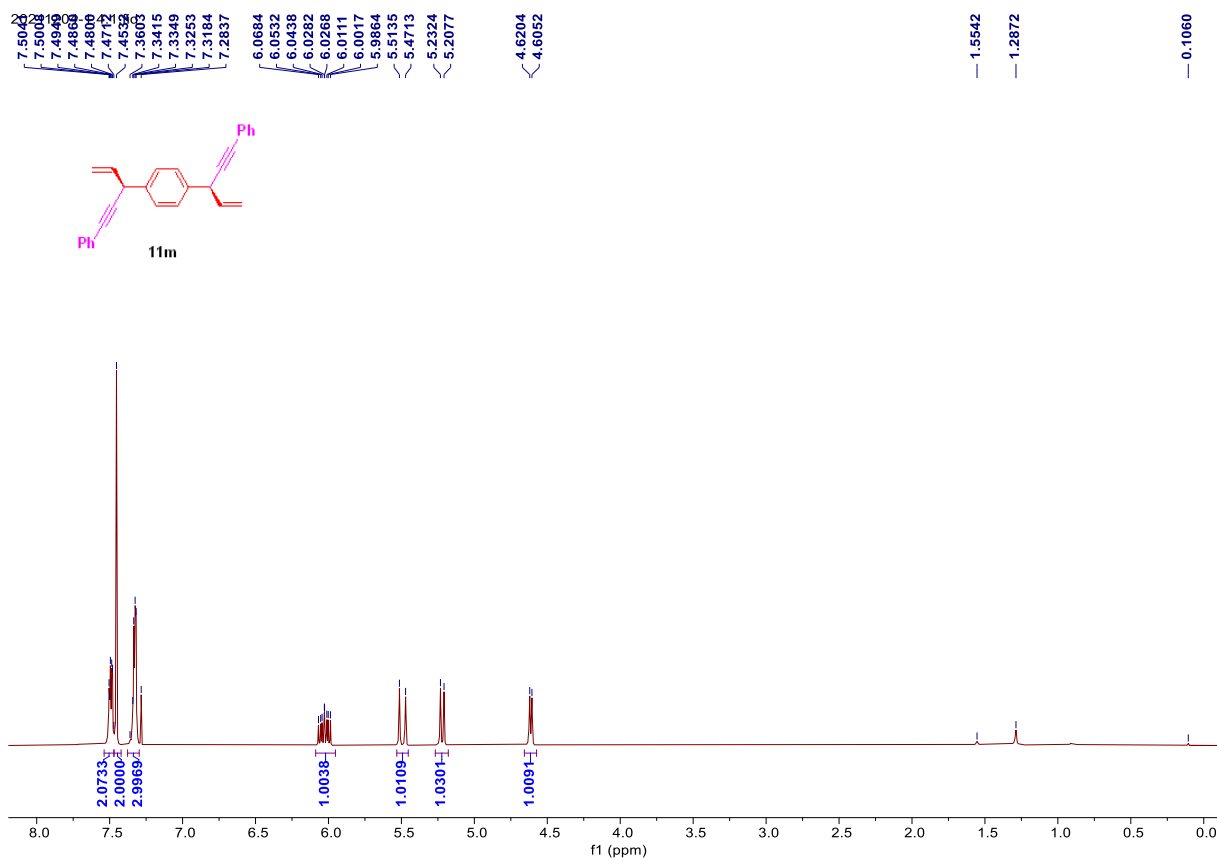
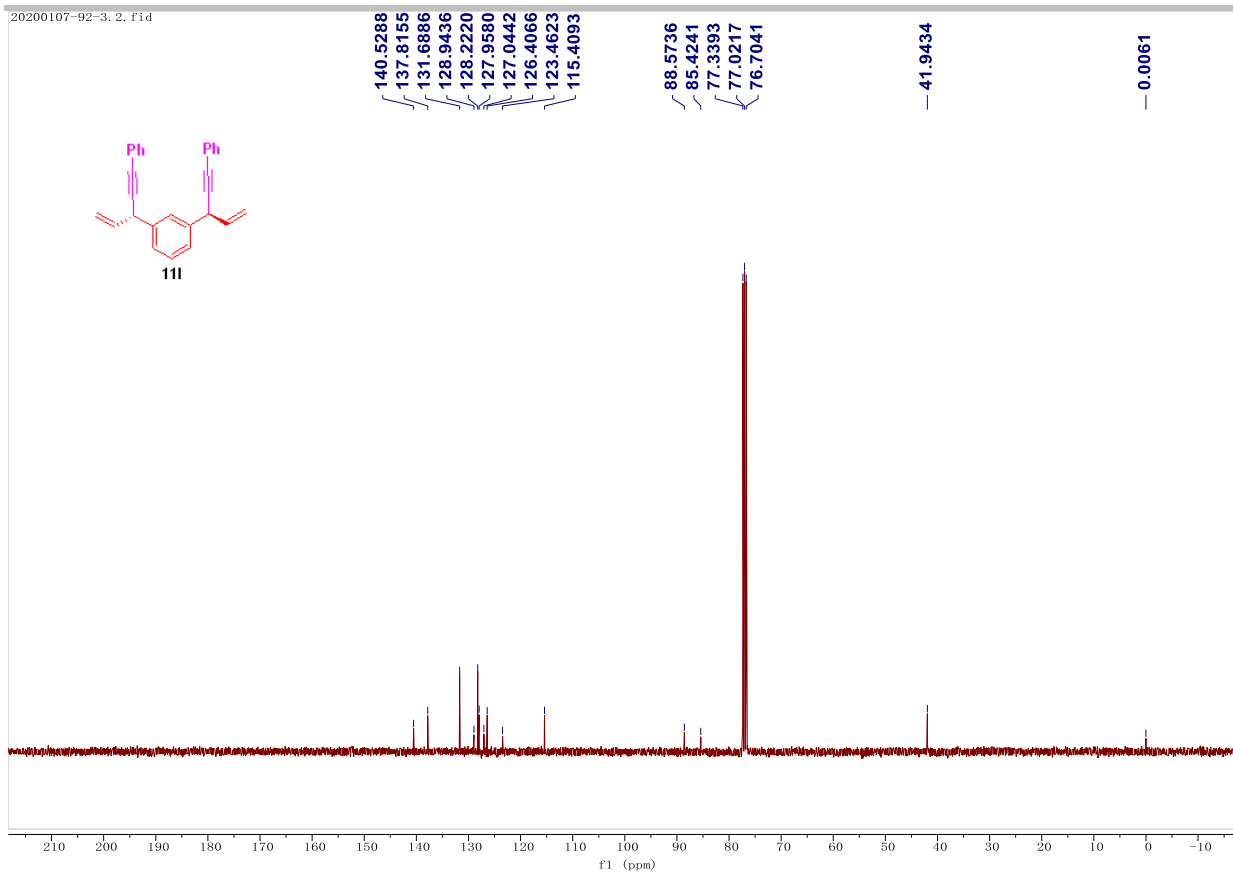


¹³C NMR (100 MHz, CDCl₃) spectrum of **11k**



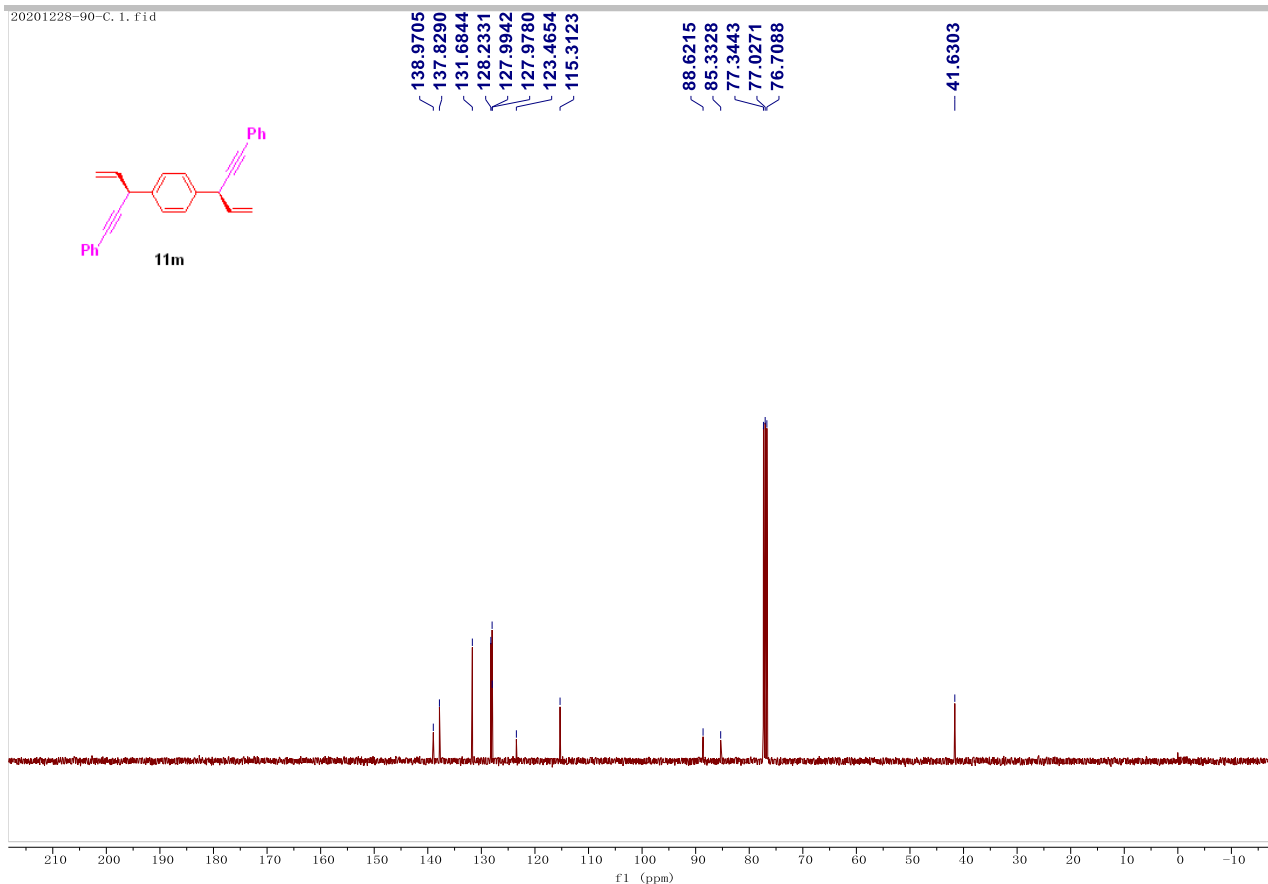
¹H NMR (400 MHz, CDCl₃) spectrum of **11l**

SUPPORTING INFORMATION

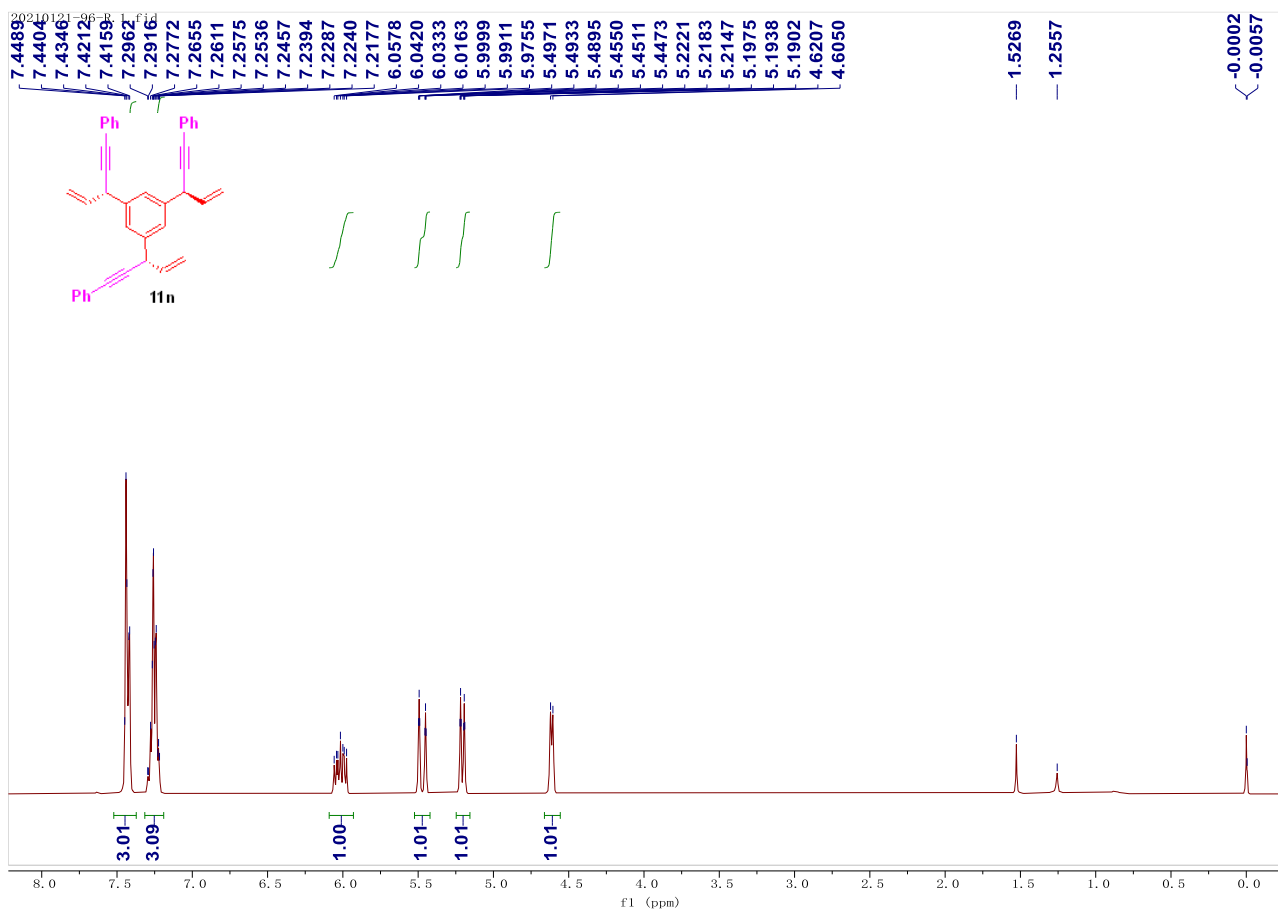


SUPPORTING INFORMATION

20201228-90-C, 1, F1d

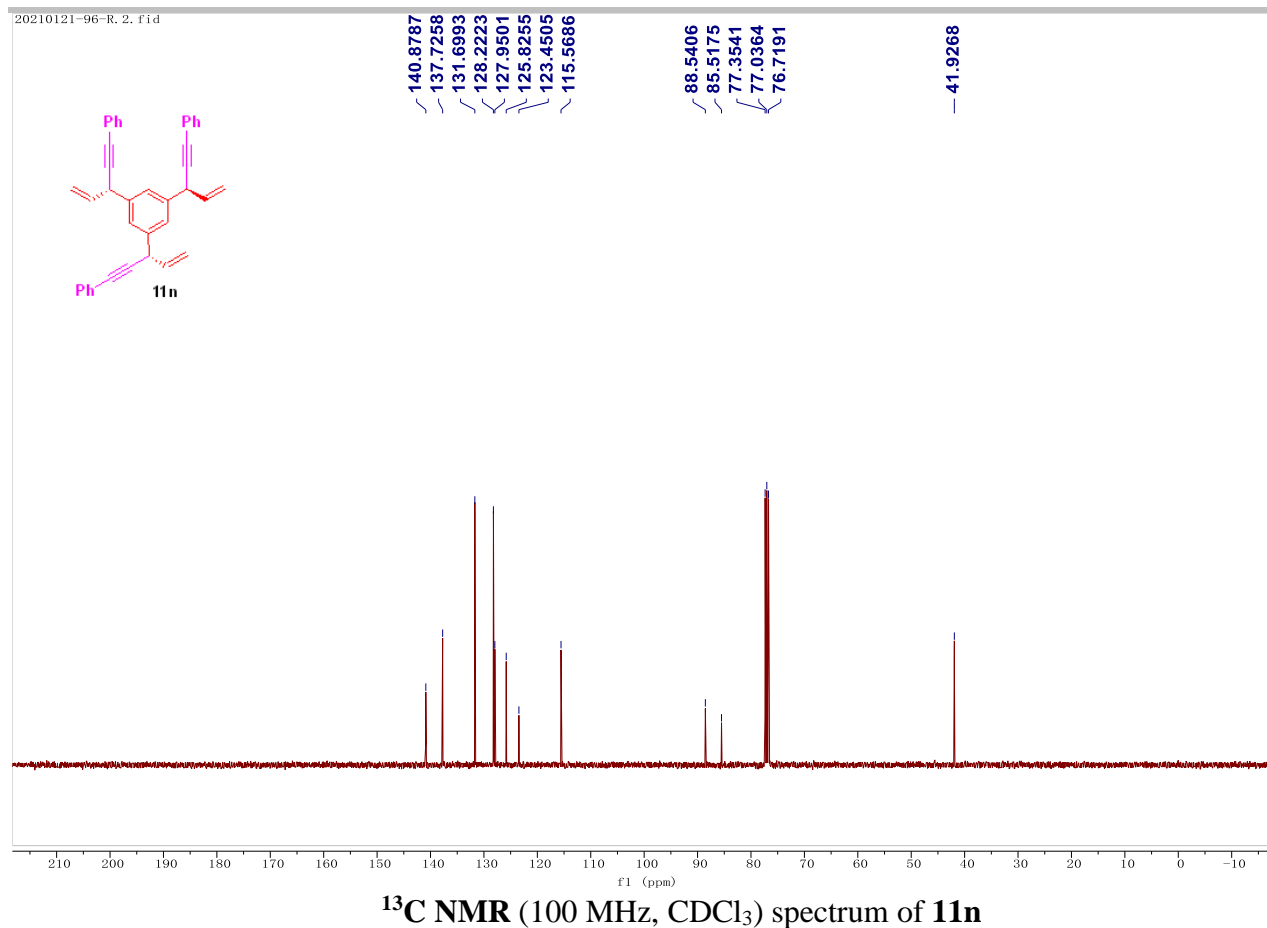


^{13}C NMR (100 MHz, CDCl_3) spectrum of **11m**



^1H NMR (400 MHz, CDCl_3) spectrum of **11n**

SUPPORTING INFORMATION



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- 2) N. Ahlsten, A. Bartoszewicz, S. Agrawal and B. Martín-Matute, *Synthesis*, **2011**, 2600-2608.
- 3) a) G. A. Molander and K. M. Traister, *Org. Lett.*, **2013**, 15, 5052-5055; b) J.-F. Wang, X. Meng, C.-H. Zhang, C.-M. Yu and B. Mao, *Org. Lett.*, **2020**, 22, 7427-7432.
- 4) J. Y. Hamilton, D. Sarlah and E. M. Carreira, *Angew. Chem. Int. Ed.*, **2013**, 52, 7532-7535.